COMPLEX OXIDE THIN FILMS AND HETEROSTRUCTURES-SCIENTIFIC OPPORTUNITIES-TECHNOLOGICAL CHALLENGES

H.-U. HABERMEIER MPI – FKF STUTTGART

OUTLINE

1. **INTRODUCTION - PHENOMENOLOGY**

   SOME COMMENTS ON COMPLEX OXIDE HETEROSTRUCTURES FERROMAGNETIC SUPERCONDUCTOR,; CUPRATE SUPERCONDUCTORS, MANGANITES, AND THEIR COMBINATION

2. **SAMPLES AND THEIR BASIC CHARACTERIZATION**

3. **OXIDE FERROMAGNET- SUPERCONDUCTOR INTERACTIONS**

   STRUCTURAL – ELECTRONIC – MAGNETIC

4. **TOWARDS AN UNIFIED VIEW**

5. **CONCLUSIONS**

COOPERATION WITH

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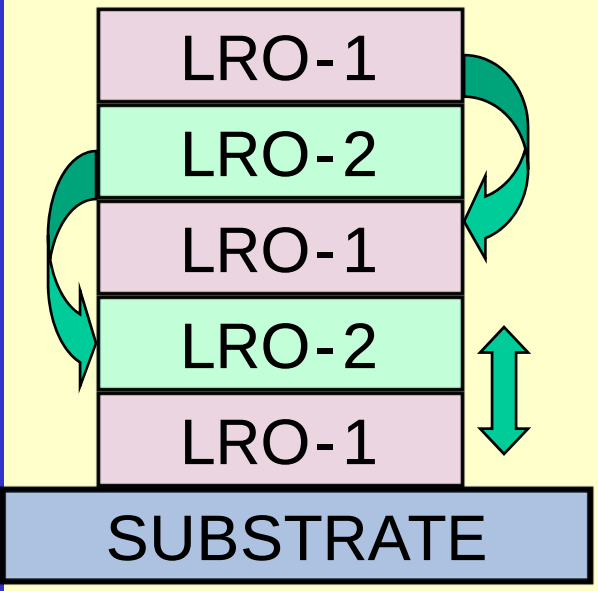
[2] University Fribourg, Switzerland

[3] University of Arkansas, Fayetteville, Arkansas, U.S.A.

[4] Bhaba Atomic Research Institute, Mumbai, India

1. INTRODUCTION – PHENOMENOLOGY (1)

COMMENTS ON OXIDE HETEROSTRUCTURES



QUESTIONS:

a.) who wins or peaceful together or mutual ignorance?

b.) crosstalk ??

c.) interfaces??

d.) construct new materials ??

ANALOGY TO METALS: Giant Magnetoresistance

Tunneling Magnetoresistance

2007 Peter Grünberg / Albert Fert

MESSAGE FROM NIKKO FOR SCIENTISTS

IF YOU CLOSE YOUR EYES AND SHUT YOUR EARS -
YOU MUST NOT TALK

BUT IF YOU TALK THEN .....

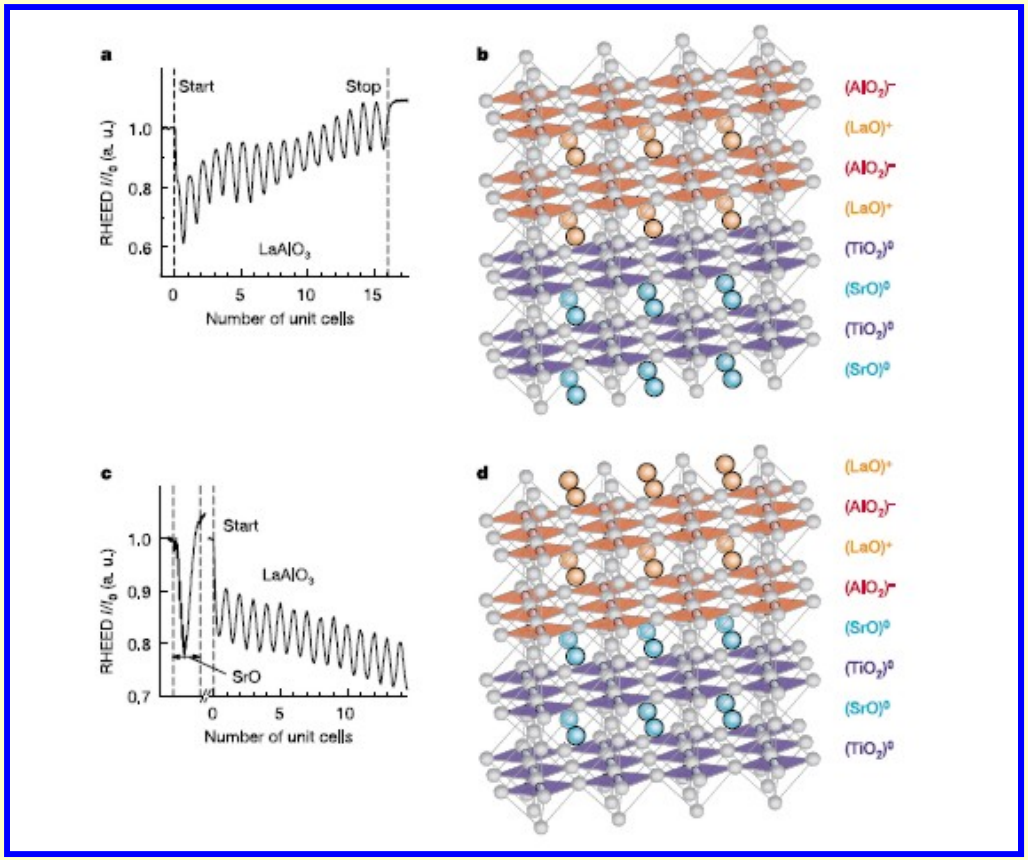
1. INTRODUCTION – PHENOMENOLOGY (2)

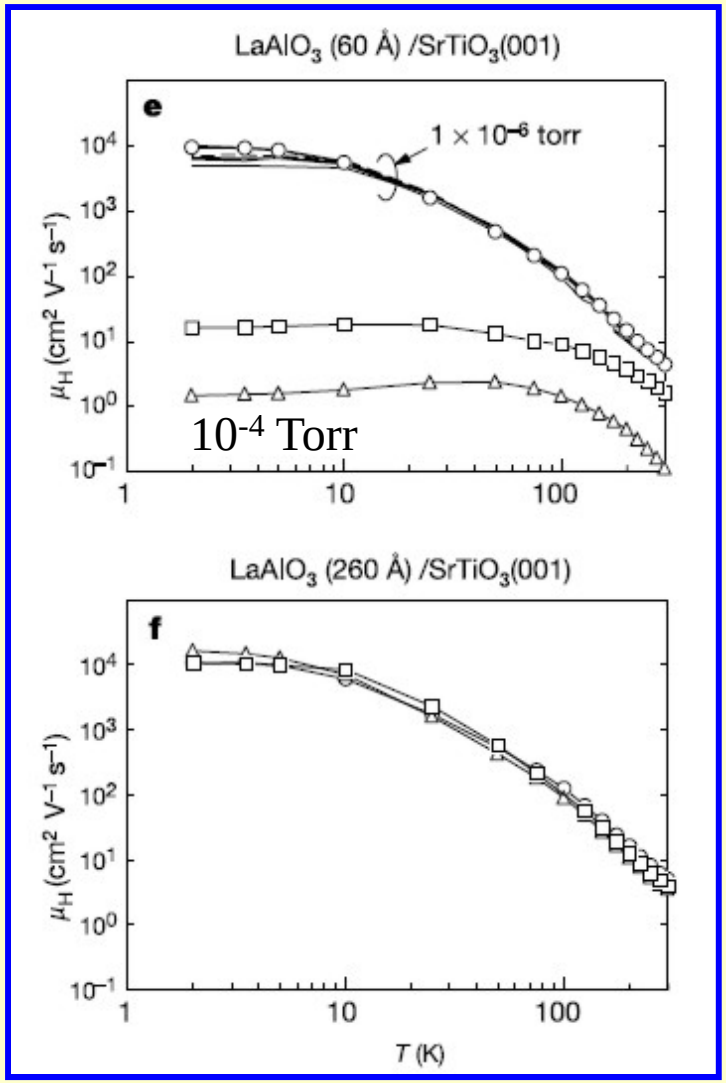
COMMENTS ON OXIDE HETEROSTRUCTURES

A high-mobility electron gas at the $LaAlO_3/SrTiO_3$ heterointerface

A. Ohtomo[1,2,3] & H. Y. Hwang[1,3,4]

Nature 427 (2004) 423

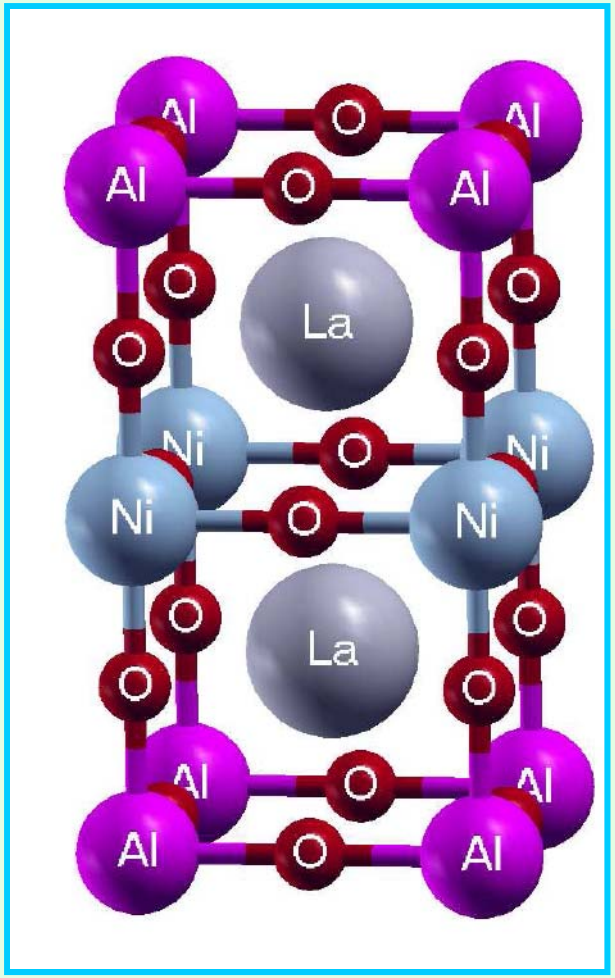


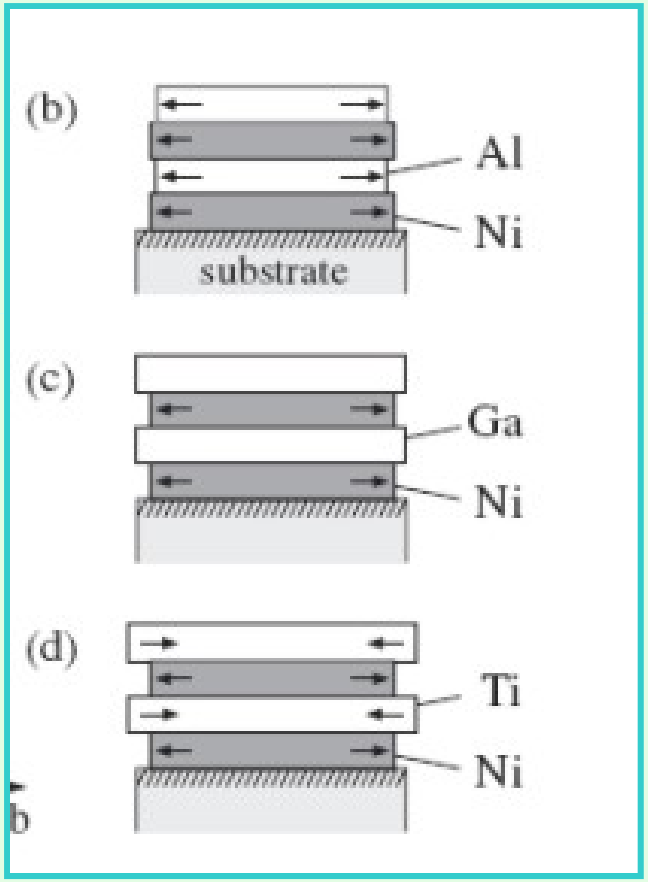


ELECTRONIC RECONSTRUCTION @ INTERFACE

G. Khaliullin PRL 100 (2008) 015404

ARTIFICIAL DOUBLE PEROVSKITES LaNiM‘O_3





Orbital Order and Possible Superconductivity in $LaNiO_3$ / $LaMO_3$ Superlattices

Jirˇí´ Chaloupka and Giniyat Khaliullin

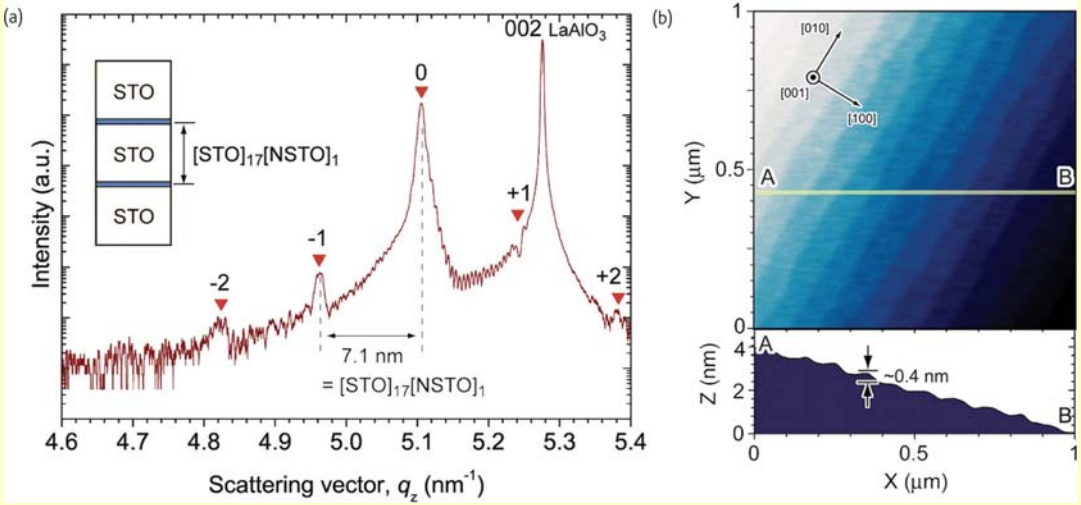
PRL **100,** 016404 (2008)

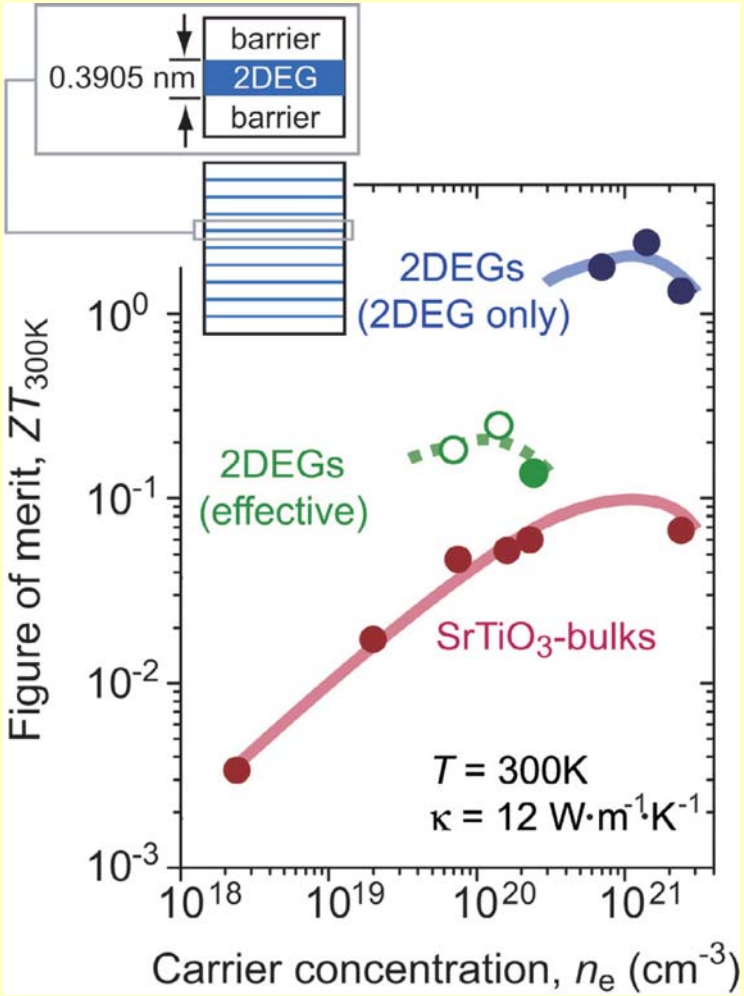
"……..that artificially tailored superlattices may open new perspectives for the high-*Tc* superconductivity. We hope that the theoretical expectations for our proposal (La_2NiMO_6) are encouraging enough to motivate experimental efforts ...."

Theorists dream → Experimentalists nightmare

THERMOELECTRICITY IN STO BASED SUPERLATTICES

H Ohta et al Nature Mat 6 (2007) 129 and Materials Today October 2007





ZT > 1@ RT

application just around the corner

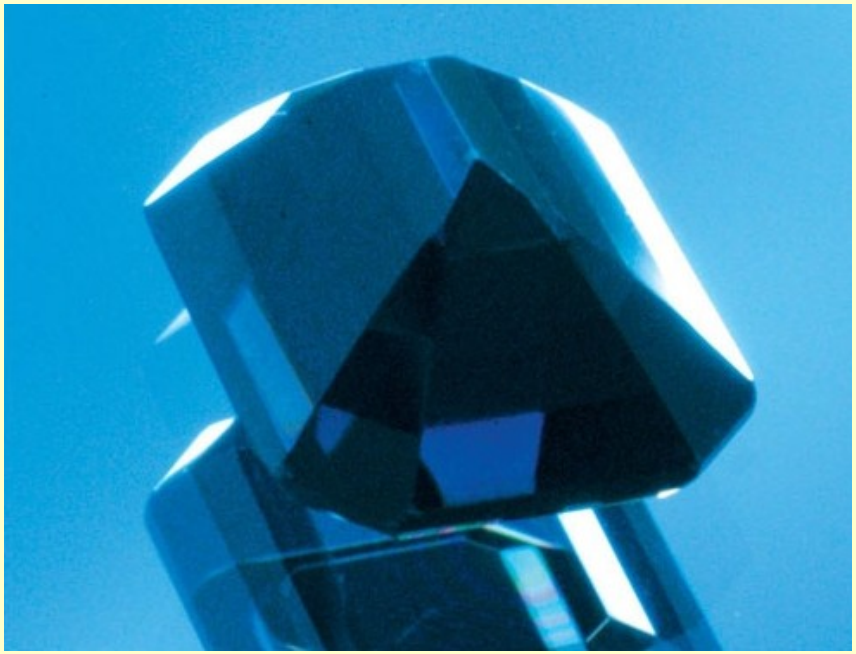
OXIDE INTERFACES

Watch out for the lack of oxygen

Interfaces between certain insulating perovskite oxides show unexpected properties, such as high conductivity and magnetism. Oxygen vacancies seem to be important in these structures, but the puzzle is far from being understood.

James Eckstein: Nature Mat. July 2007

$SrTiO_3$ and oxygen

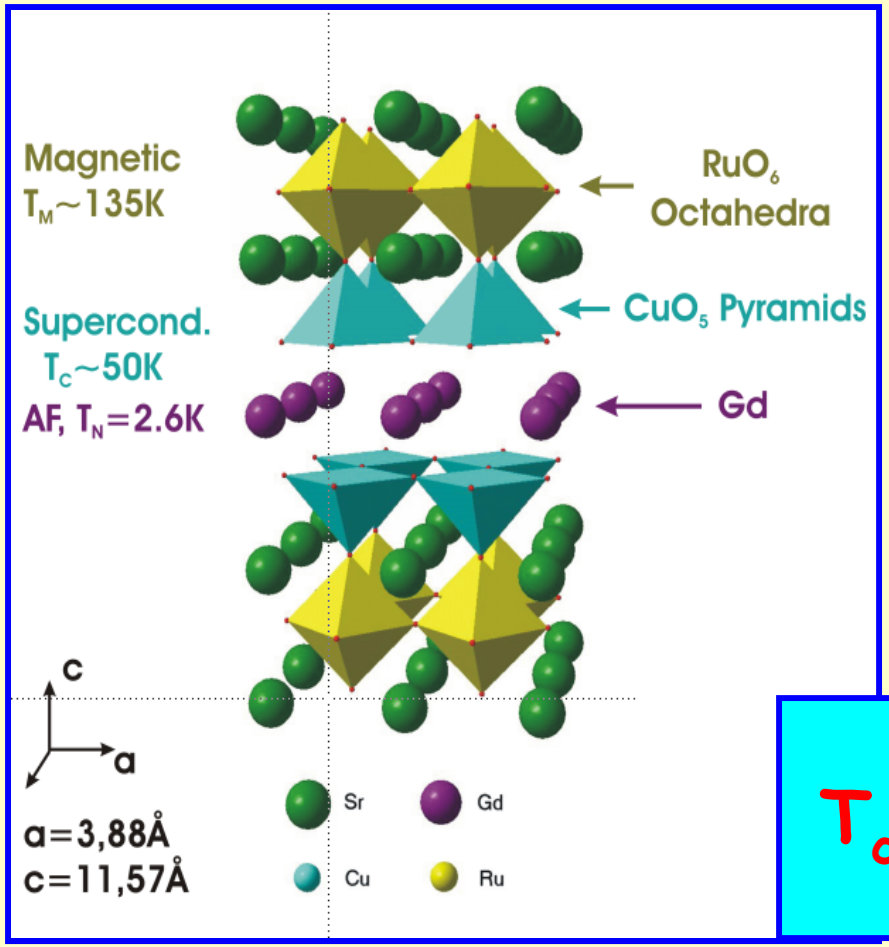


PHENOMENOLOGY (3)

COMMENTS ON FERROMAGNETIC SUPERCONDUCTORS, CUPRATE SUPERCONDUCTORS, MANGANITES, AND THEIR COMBINATION

FERROMAGNETIC SUPERCONDUCTORS

Ruthenocuprates e.g. $RuSr_2GdCu_2O_8$



DISCOVERY: L. Bauernfeind and H. F. Braun Physica C 254, 151 (1995).

COEXISTENCE of FM and SC

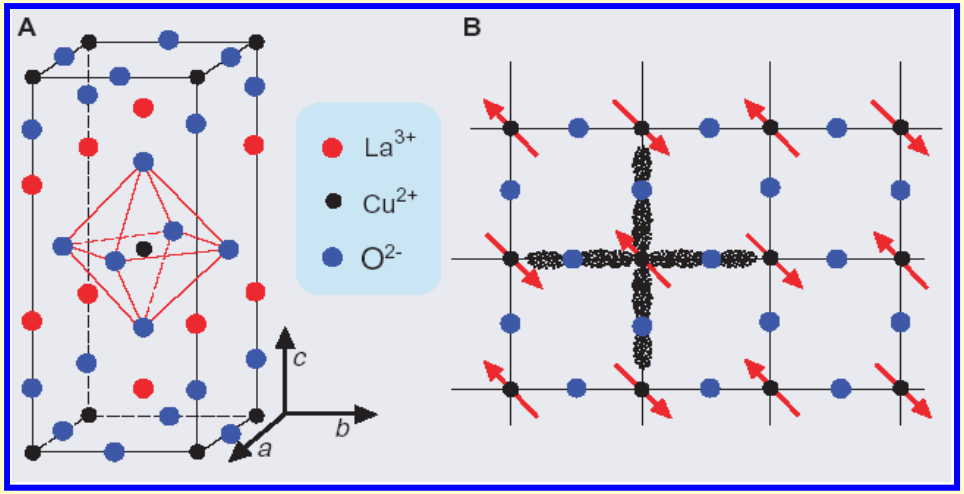
Ch. Bernhard et al., Phys. Rev. B 59, 14099 (1999)

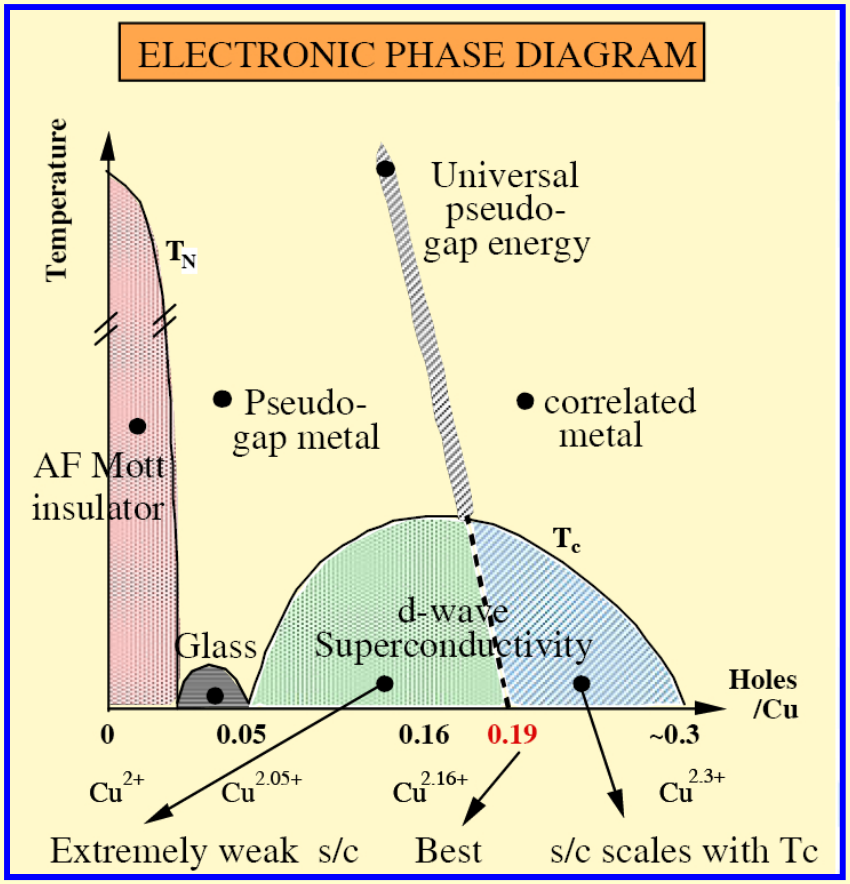
FM vs. AFM J.W. Lynn *et. al.* Phys. Rev. B 61, R14964 (2000)

THIN FILMS O. I. Lebedev, H.-U. H et al. Phys. Rev. B. 71 (2005) 134523

T_c and T^{Curie} < bulk values

CUPRATE SUPERCONDUCTORS





Perovskite-type structure

Antiferromagnetic ground state

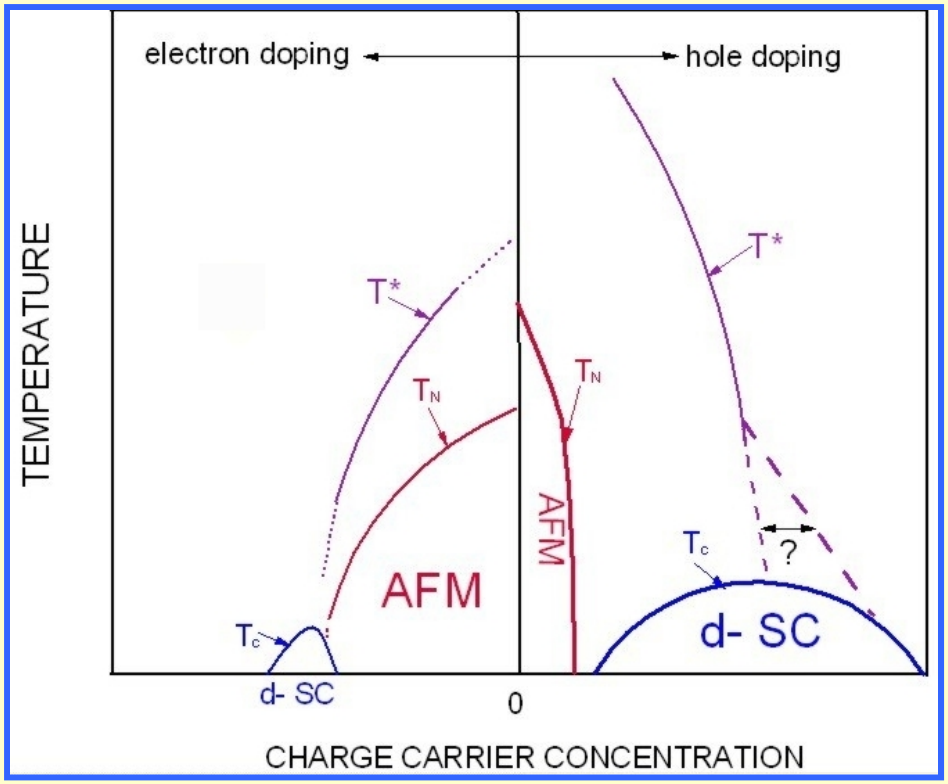
d- wave symmetry of order parameter

T_c and conductivity sensitively depend on CuO_2 plane doping

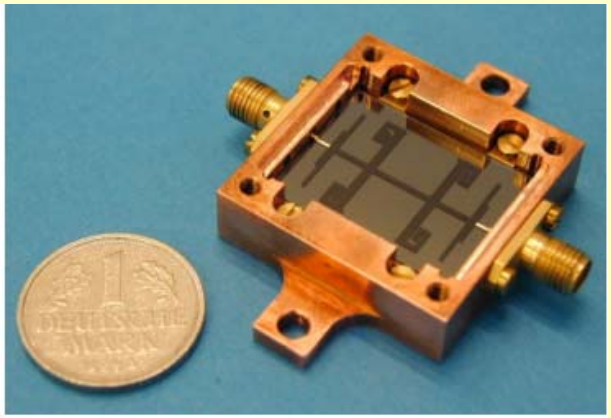
WHAT REMAINS IN HTS RESEARCH AFTER 20 YEARS??

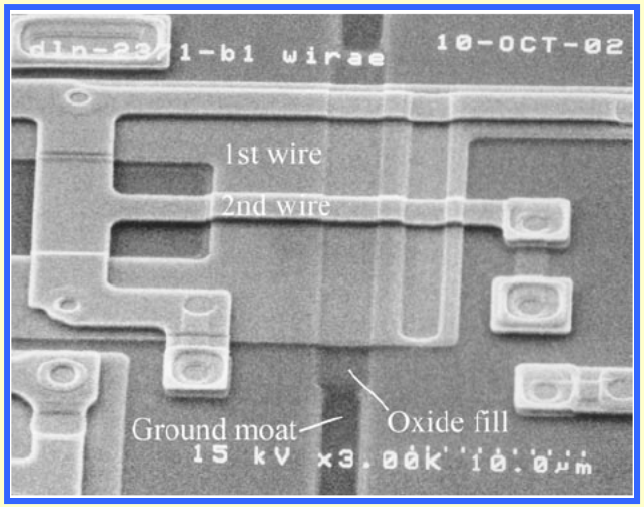
MECHANISM(S) CAUSING HIGH T_c

ROLE OF PSEUDOGAP



EXPLORATION OF HTS APPLICATION POTENTIAL

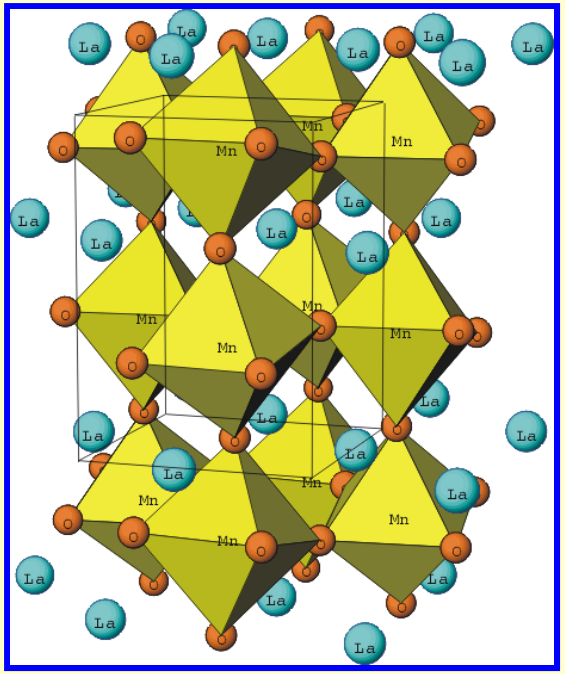


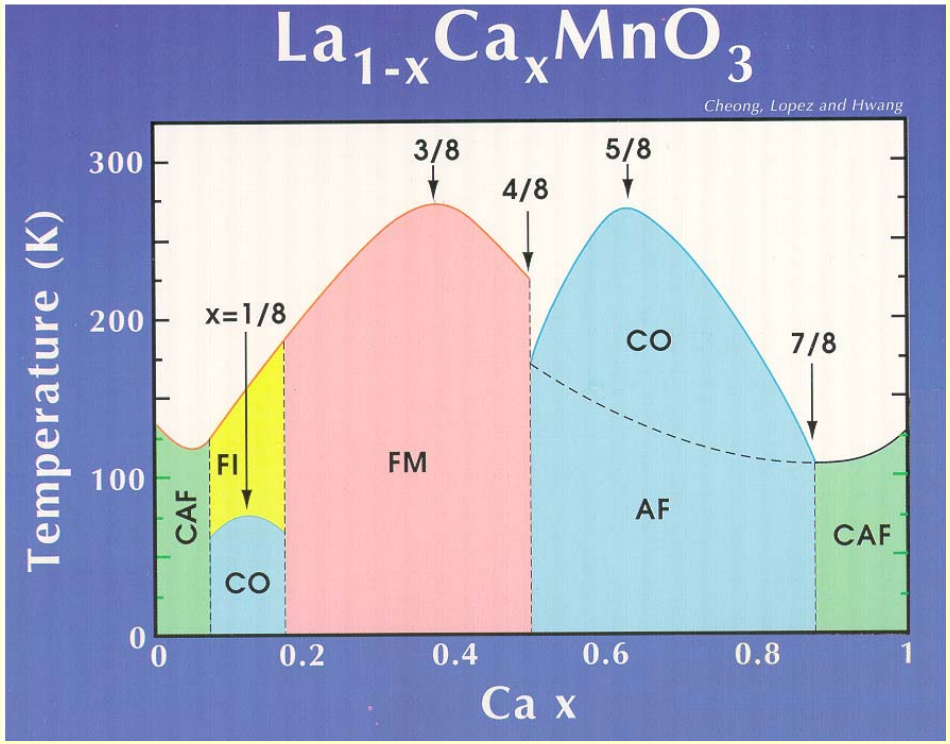


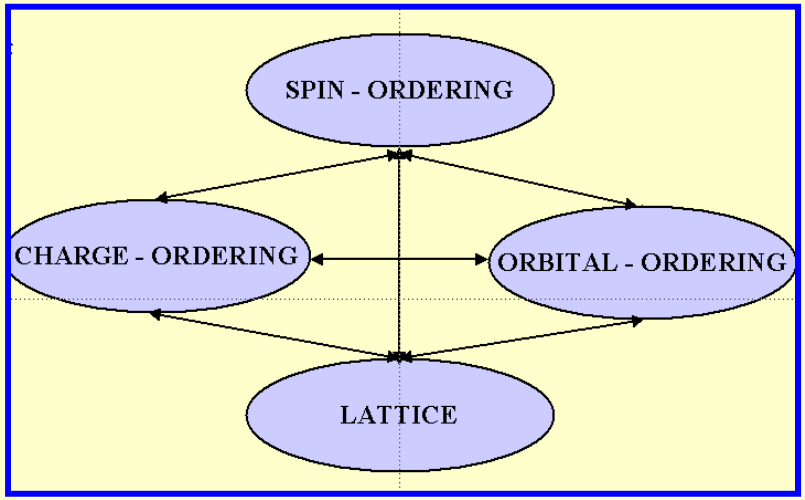
Buddhist Udana 100 BC

6 blind men and the elephant

FERROMAGNETIC MANGANITES







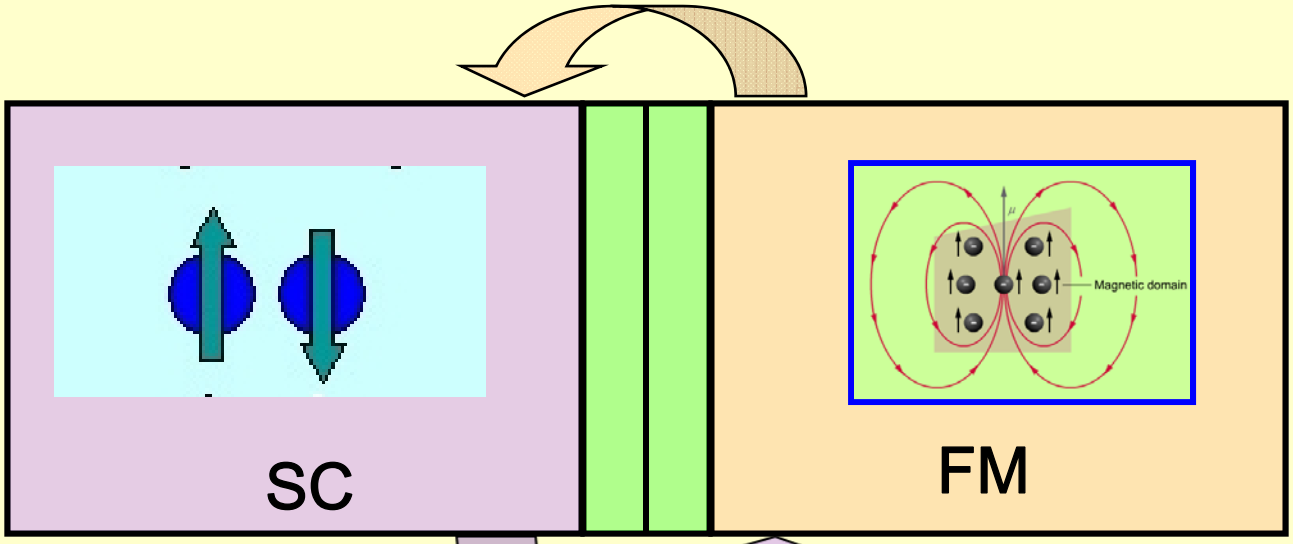
Perovskite-type structure

Doping dependent magnetic ground state

100% spin-polarization of e_g electrons

Spin-Charge-Orbital-Lattice coupling

FERROMAGNET- SUPERCONDUCTOR OXIDE INTERFACE



INTERACTION AT INTERFACE

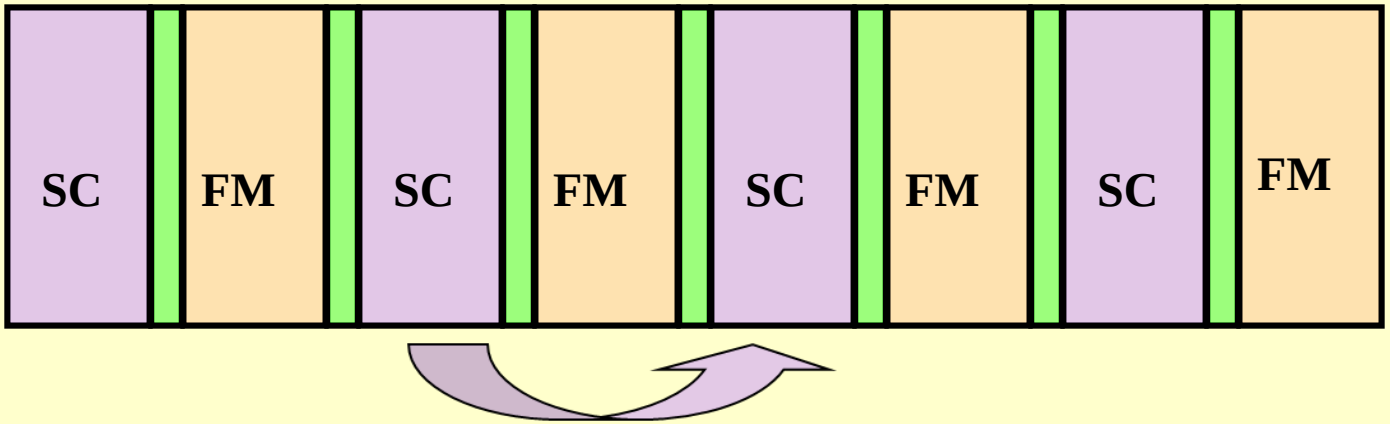
New groundstate

New properties

New material

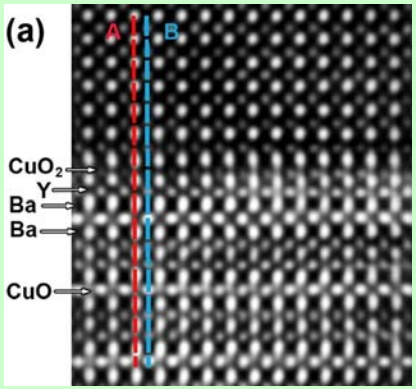
?

INTERACTION ACROSS FM (SC) LAYER



WHY IS THAT INTERESTING ??

FUNDAMENTALLY



LCMO

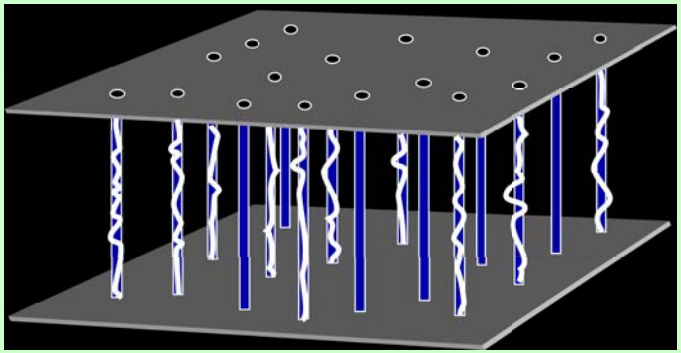
YBCO

Electronic Structure @ Interface ?

Consequences of its modification, if any ?

Is something new emerging ?

PRACTICALLY



Are 1 D artificial (oxide) pinning centers only non-SC precpitates ?

What, if they are FM ?

What, if they form regular structures ?

GOAL

USE CUPRATE MANGANITE HETEROSTRUCTURES AND SUPERLATTICES AS PROTOTYPE MATERIALS TO STUDY THE INTERACTION OF OXIDES WITH DIFFERENT FUNCTIONALITIES

FOCUS ON ROLE OF THE INTERFACE

ACTIVITIES INITIATED BY

G. Jakob et al. Appl. Phys. Lett 66 (1995) 2564

P. Przyslupski et al. IEEE Trans. Appl. Superc. 7, 2192 (1997)

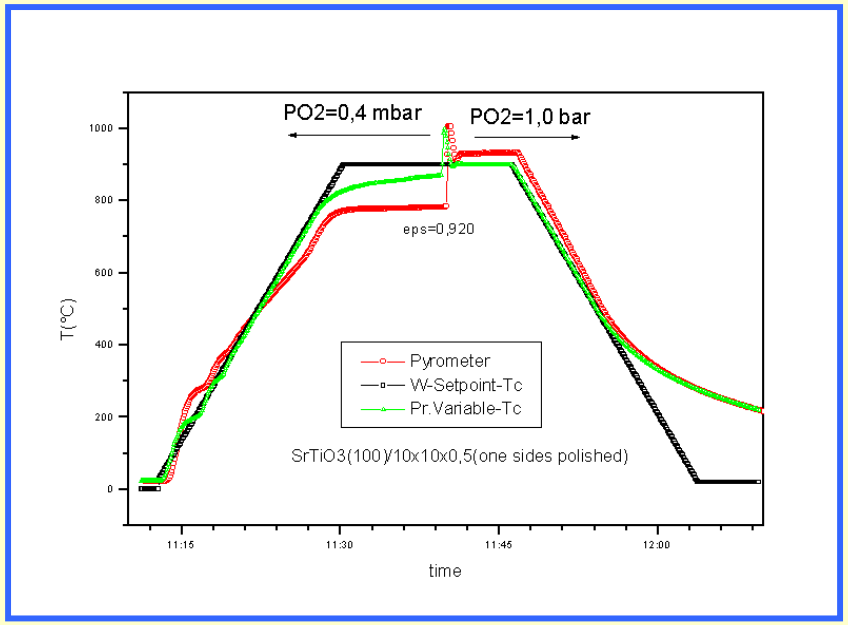
P. Prieto, P. Vivas, G. Campillo, E. Baca, L. F. Castro, M. Varela, C. Ballesteros, J. E. Villegas, D. Arias, C. Leon, and J. Santamaria,
J. Appl. Phys. 89, (2001) 8026

H.-U. Habermeier et al. Physica C 354, (2001) 298

2. SAMPLE PREPARATION AND CHARACTERIZATION

PULSED LASER DEPOSITION

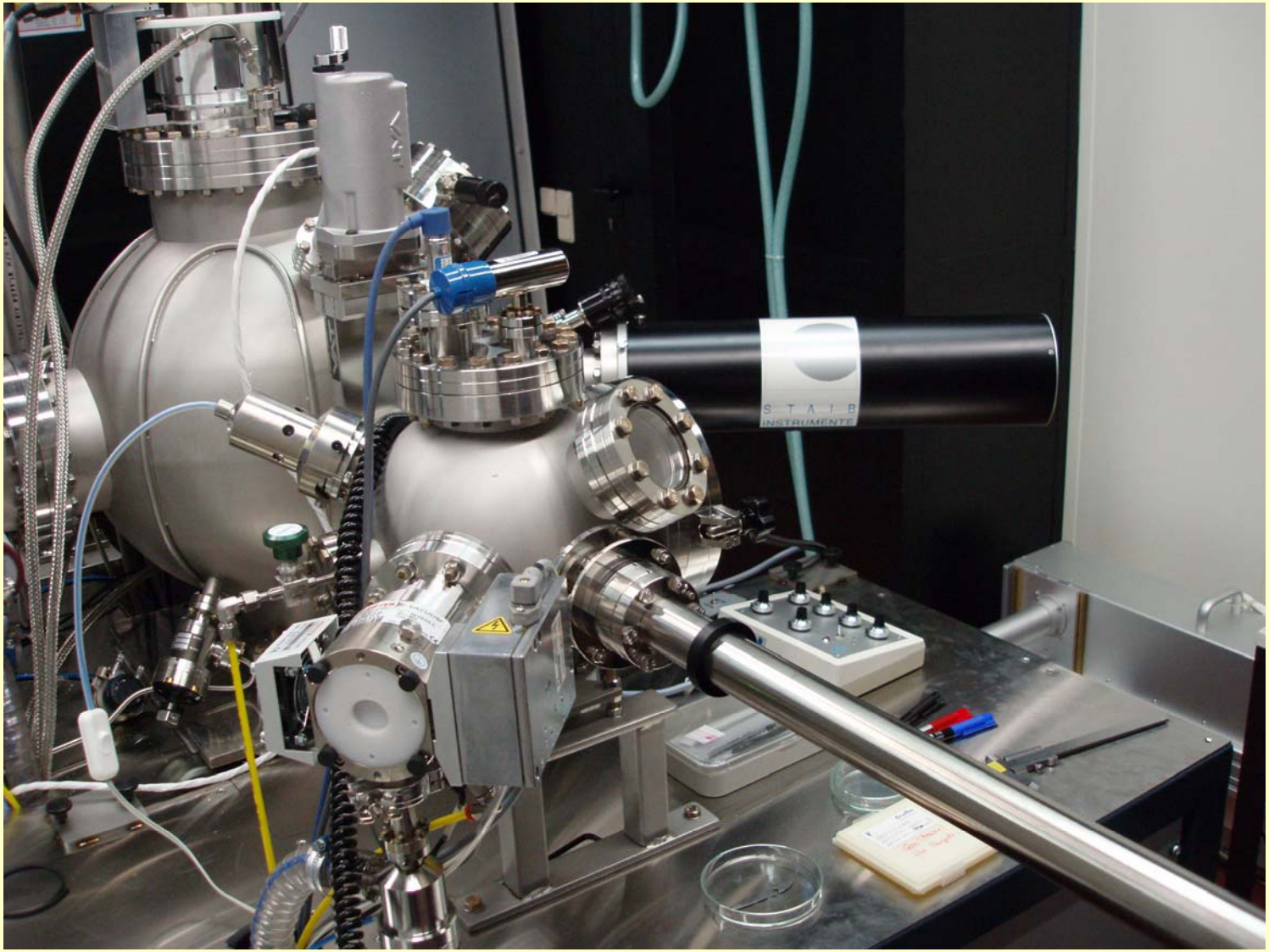
KrF - Excimerlaser 248 nm
Oxygen: .5 mbar
Computer - controlled target exchange



Pyrometric temperature control

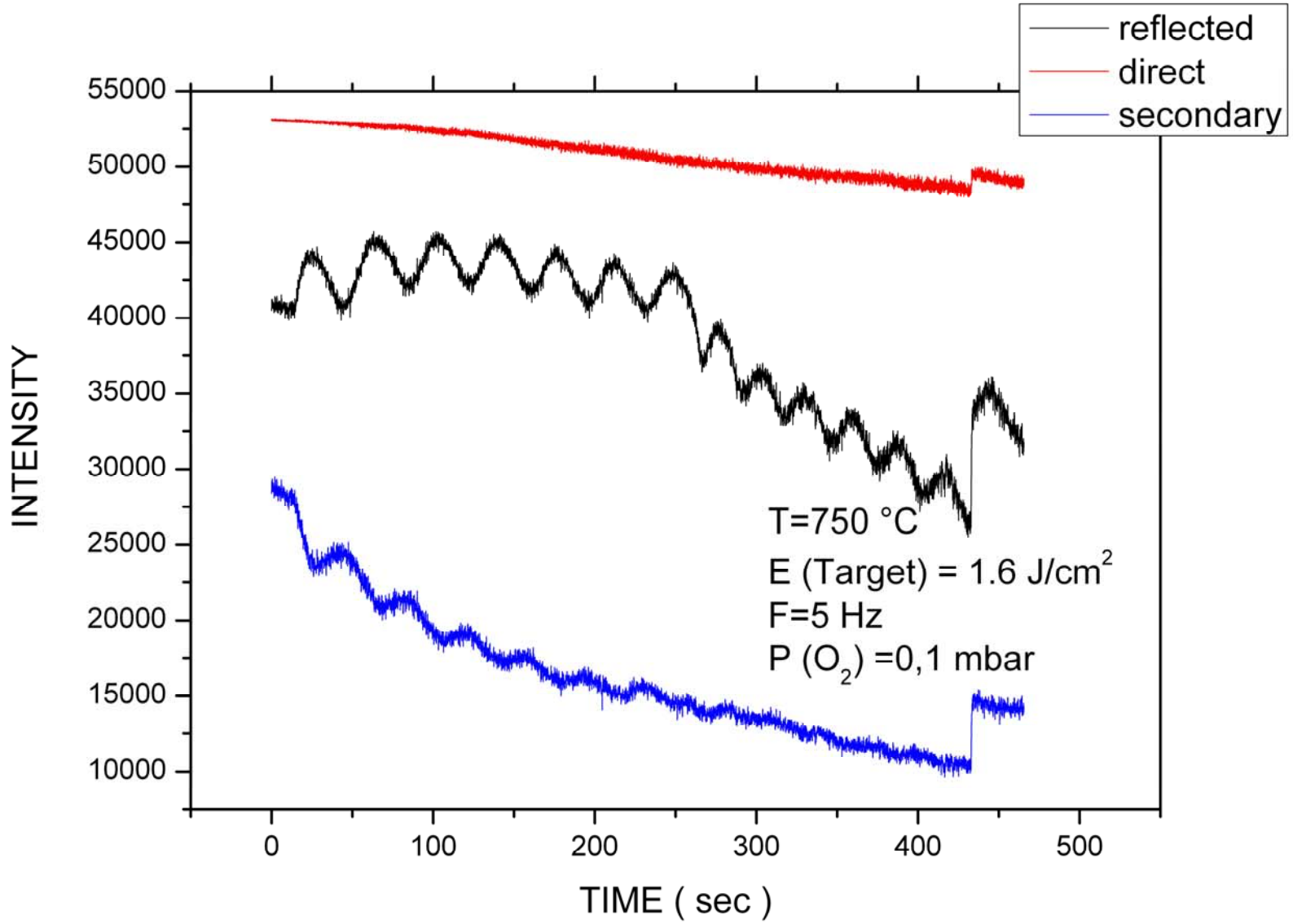
180nm YBCO dep. rate ~15 nm/min

Total high T exposure < 20 min

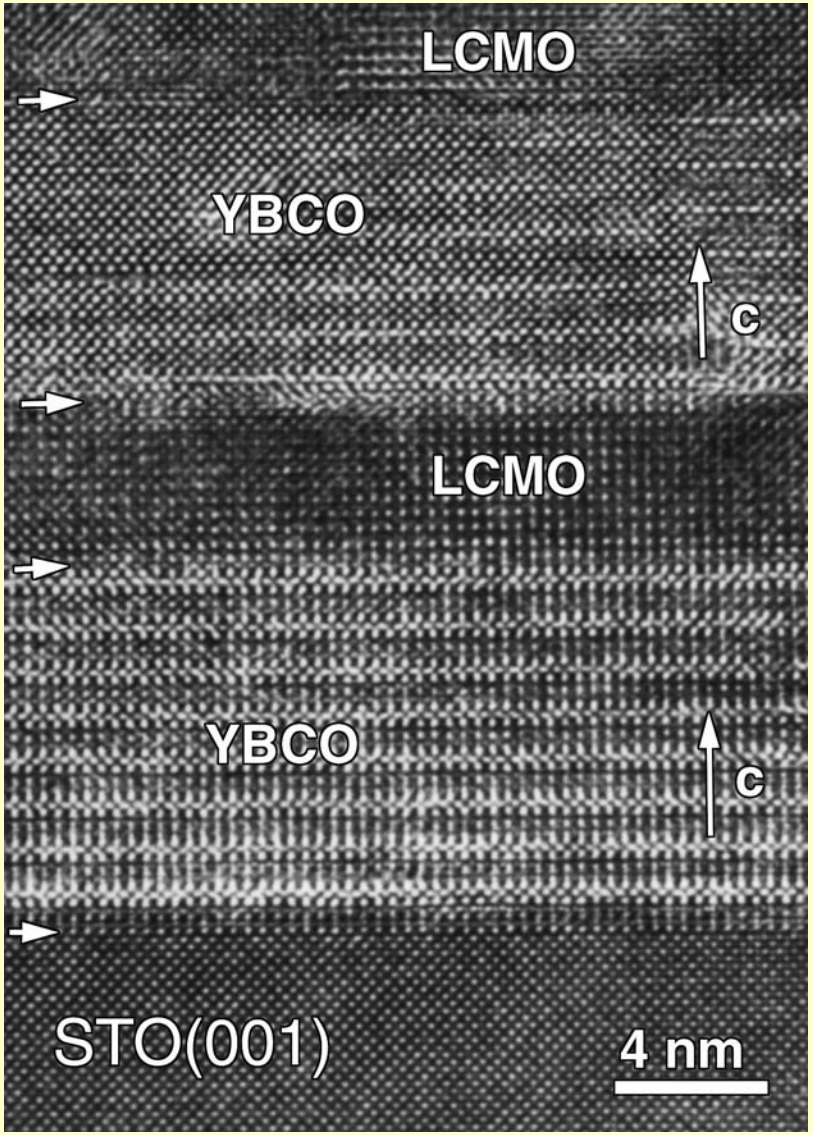


UHV – PLD SYSTEM WITH RHEED and TRANSFER-CHAMBER

THIN FILM GROWTH CONTROL BY RHEED

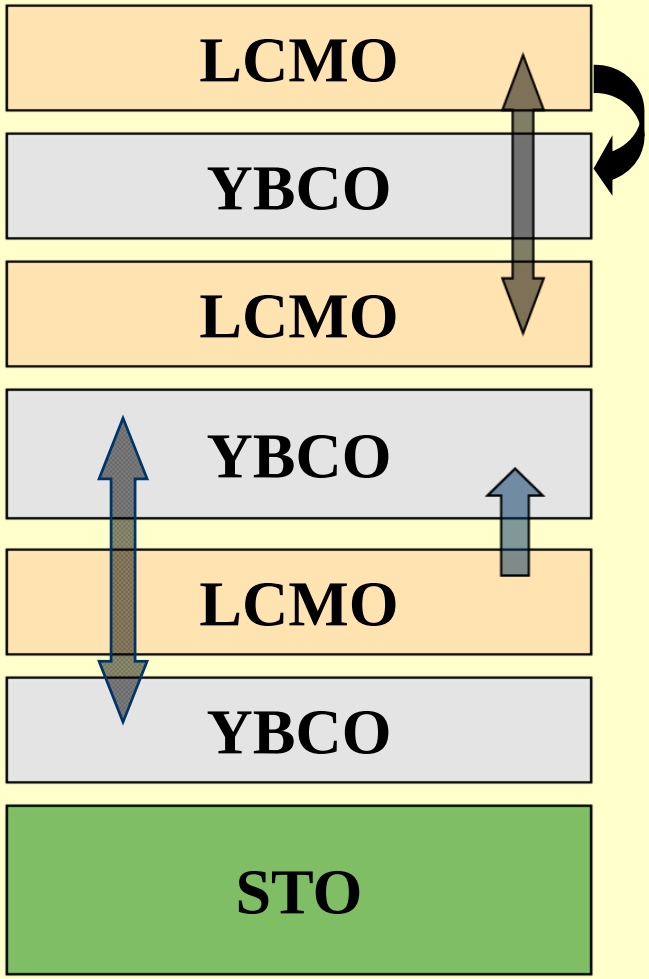


HRTEM YBCO /LCMO



3. OXIDE FERROMAGNET- SUPERCONDUCTOR INTERACTIONS

STRUCTURAL – ELECTRONIC – MAGNETIC



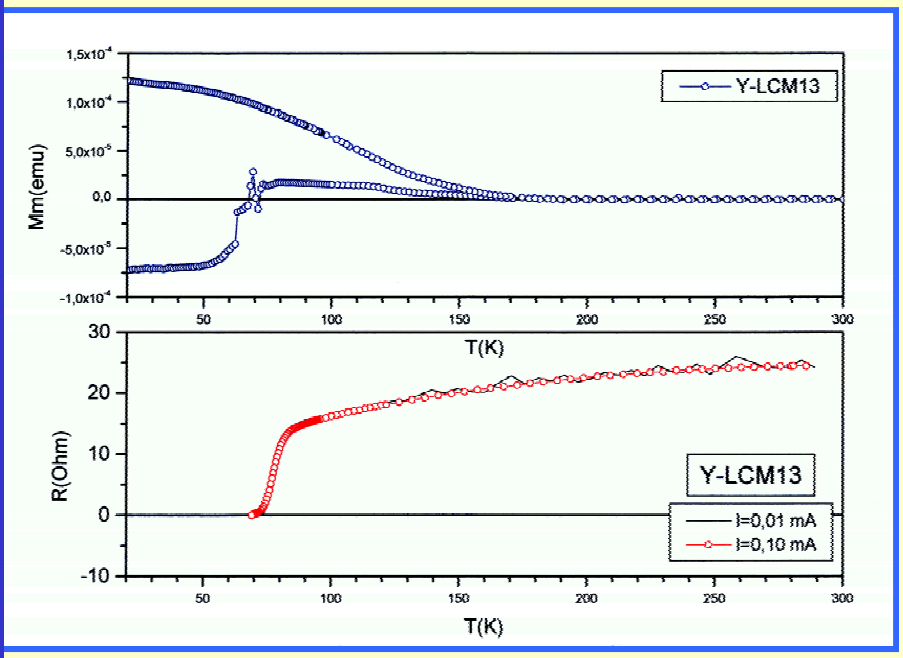
Charge Transfer Santamaria, Varela et al.

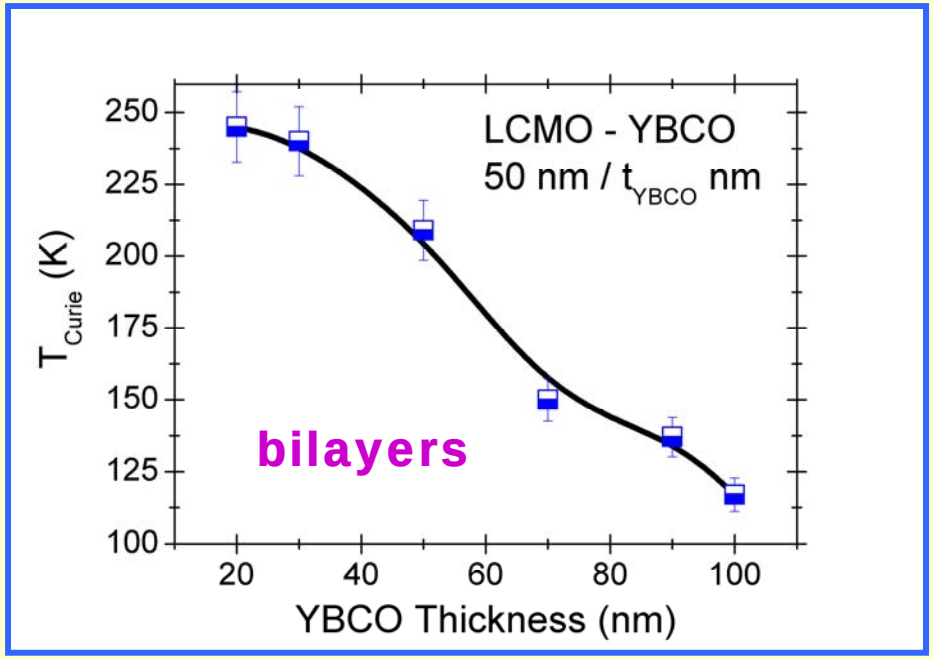
Diffusion of spinpolarized quasiparticles
Soltan et al.

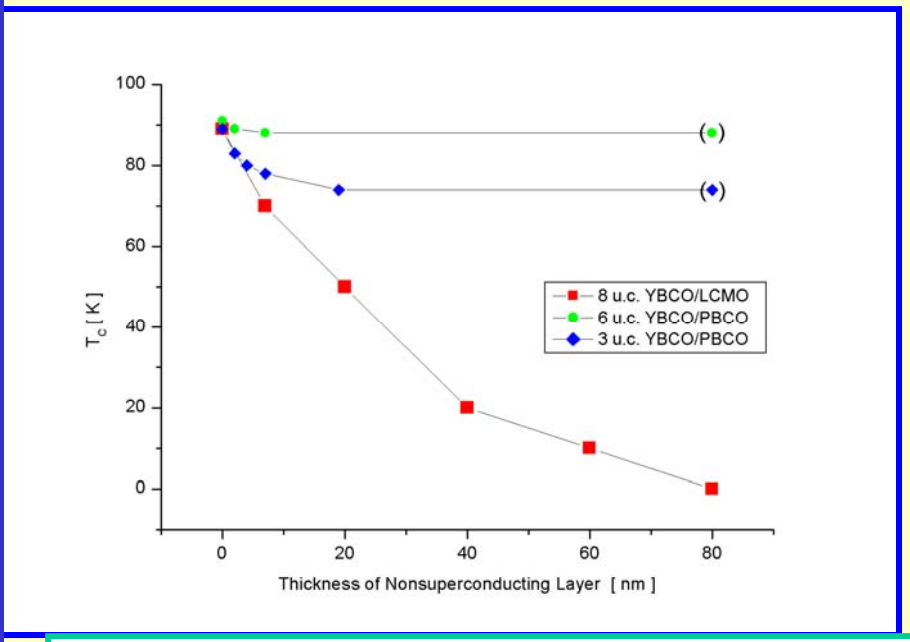
Proximity effect coupling via YBCO
Bulaevski, Efetov …. Sa de Melo

Magnetic proximity effect Bergeret, Efetov

Coupling via FM spacer



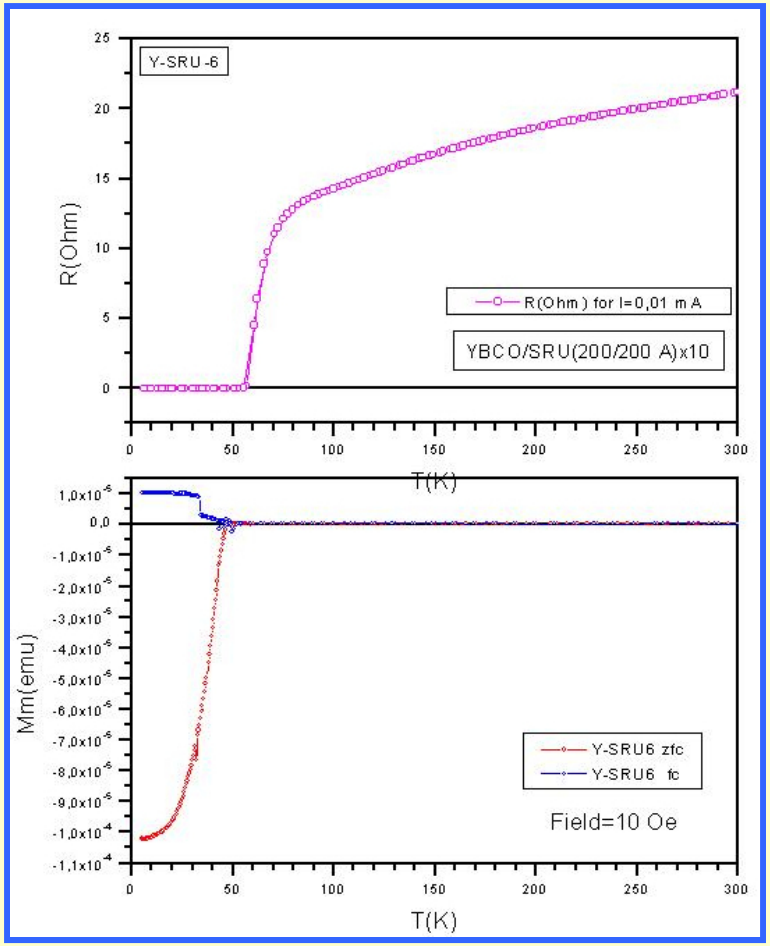


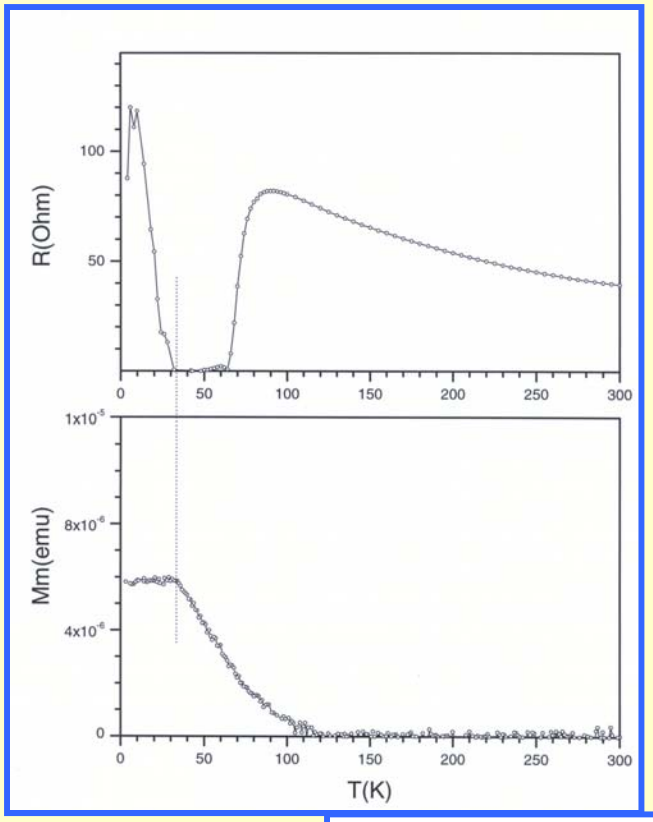


- depression of T^{Curie} and T_c
- magnetism matters
- "superconductivity" matters

  - regime of pseudogap ?? -

H.-U. H., G. Christiani et al. Physica C 364 (2001) 298 H.-U. H. and G. Christiani J. of Supercond. 15 (2002) 425

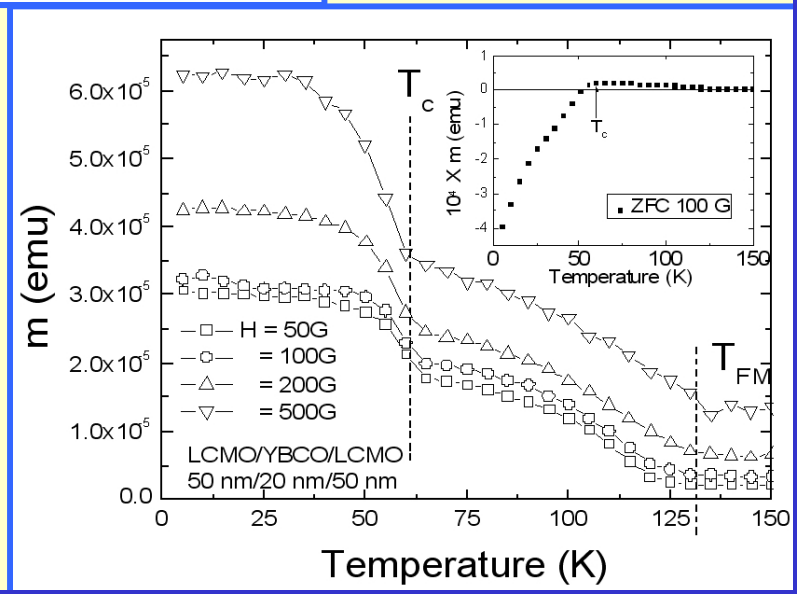


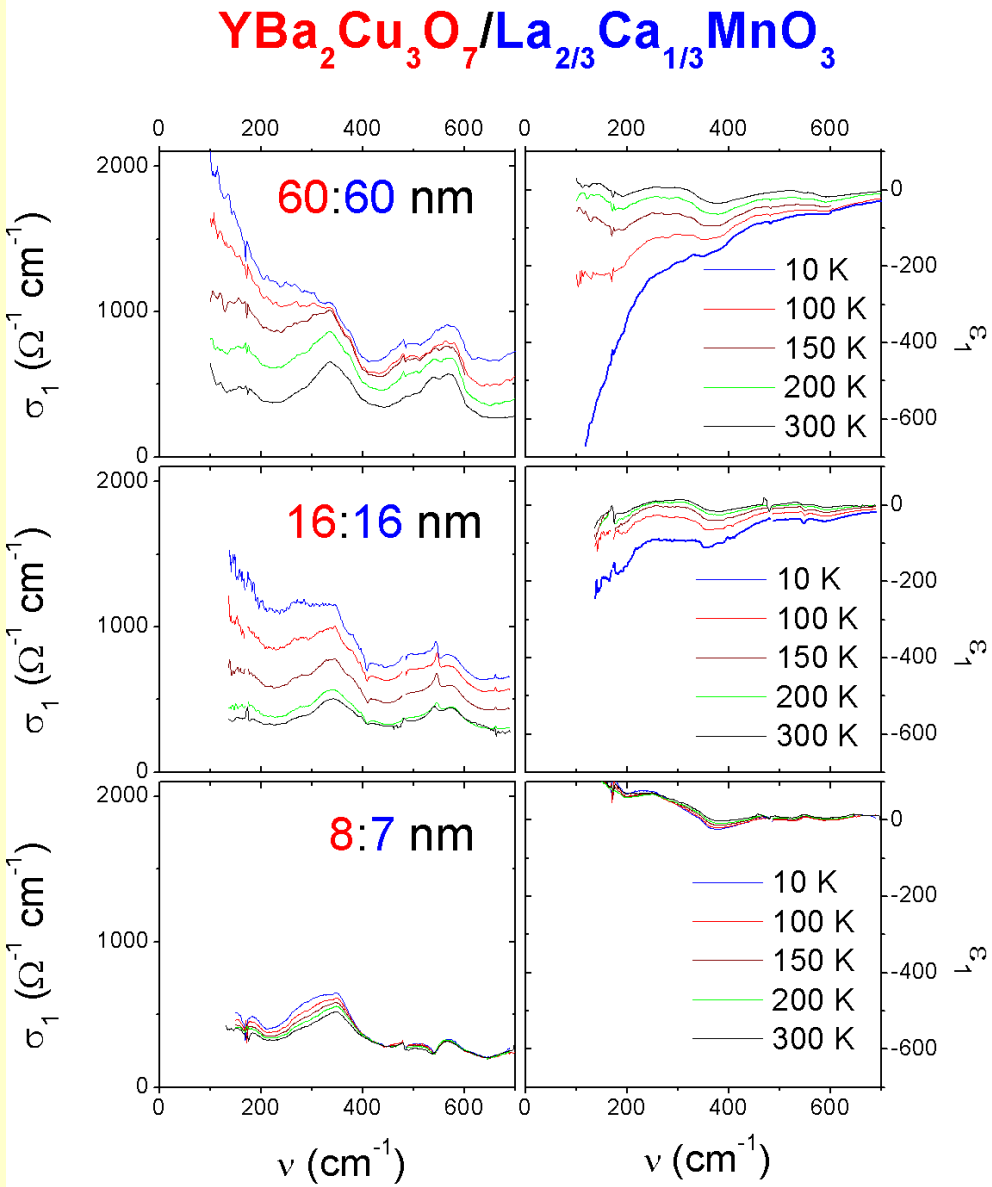


YBCO- LCMO
5nmx5nm
superlattice

YBCO-SRO 20nmx20nm
superlattice

- magnetic coupling across the SC spacer





SPECTROSCOPIC ELLIPSOMETRY

T_c=85 K; T^{mag}=245 K

T_c=73 K; T^{mag}=215 K

T_c=60 K; T^{mag}=120 K

strange metal (SC) + strange metal (FM) ⇒ strange insulator

T. Holden, C. Bernhard, H.-U. H. *et al.*, Phys. Rev. B 69, (2004) 064505

CHARGE REDISTRIBUTION AT INTERFACE

Distance for movement of charges is given by Thomas Fermi screening length

$$\lambda_{TF} = \frac{1}{2}\sqrt{\frac{a_0}{n^{1/3}}}$$

Bohr radius

Charge carrier density

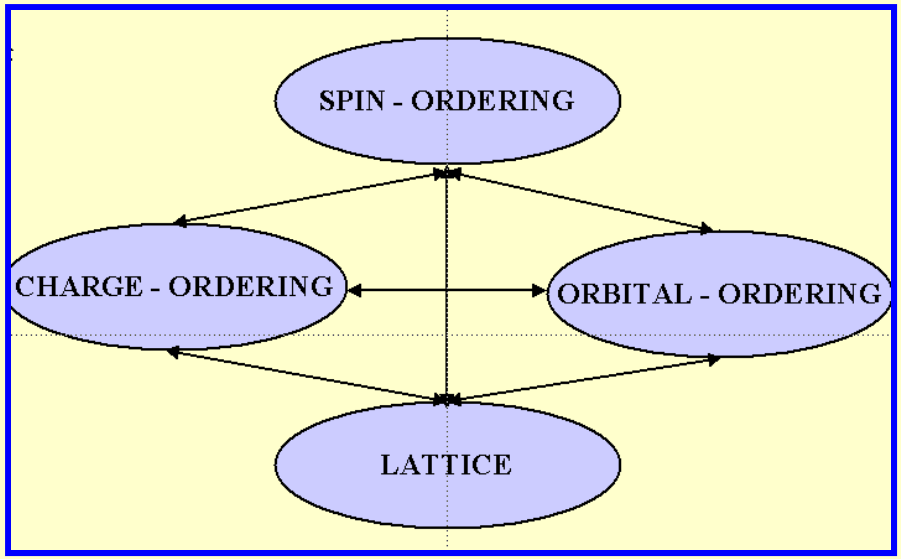
Typically 10^{19}-10^{22} cm^{-3} in complex oxides

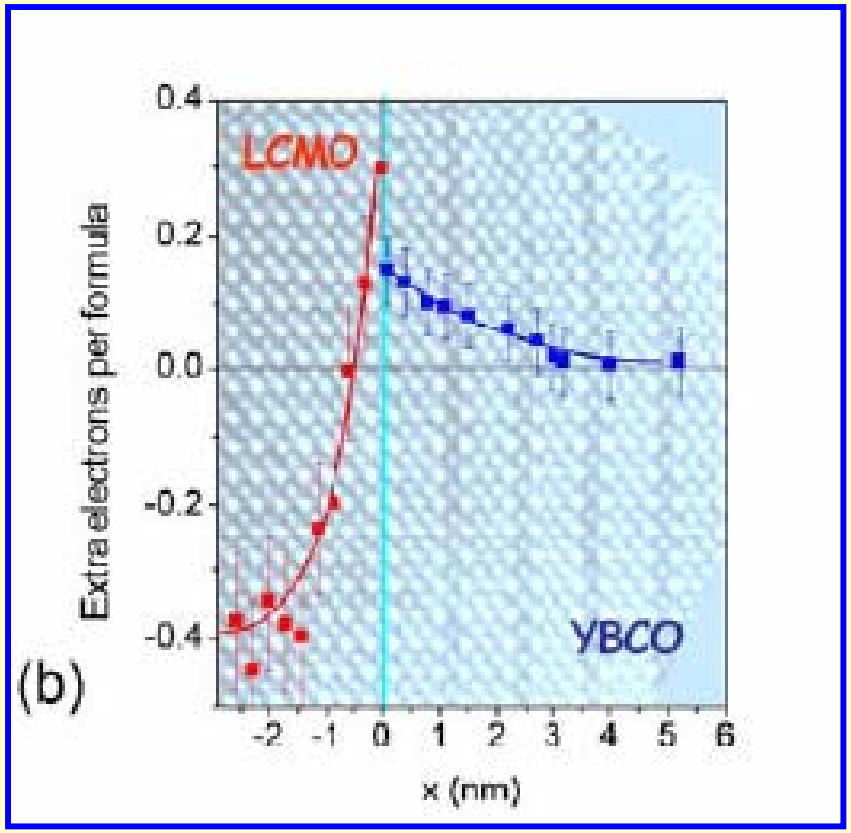
λ_{TF} = 2 – 6 Å (1–2 unit cells)

EXPERIMENTALLY: STEM- EELS STUDIES

M. Varela, S. Pennycock, J. Santamaria et al.. cond-mat 0508564

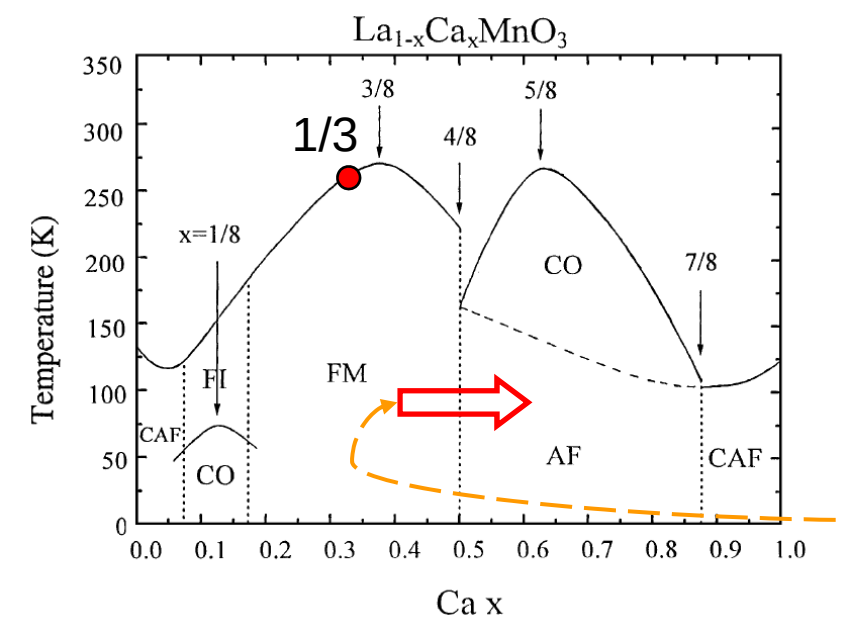
Amount of excess (depleted) electrons per formula within the YBCO (LCMO) layers as a function of distance along the growth direction, as measured from EELS.



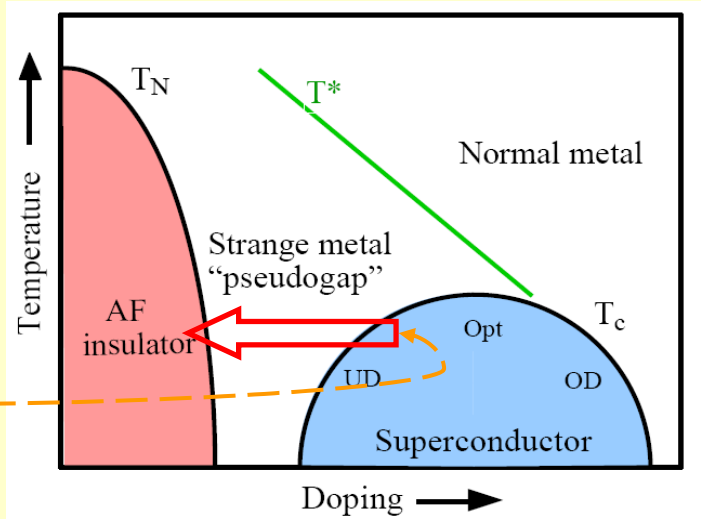


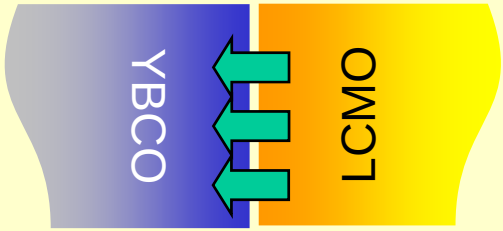
PHASE DIAGRAMS

Charge Transfer across the interface



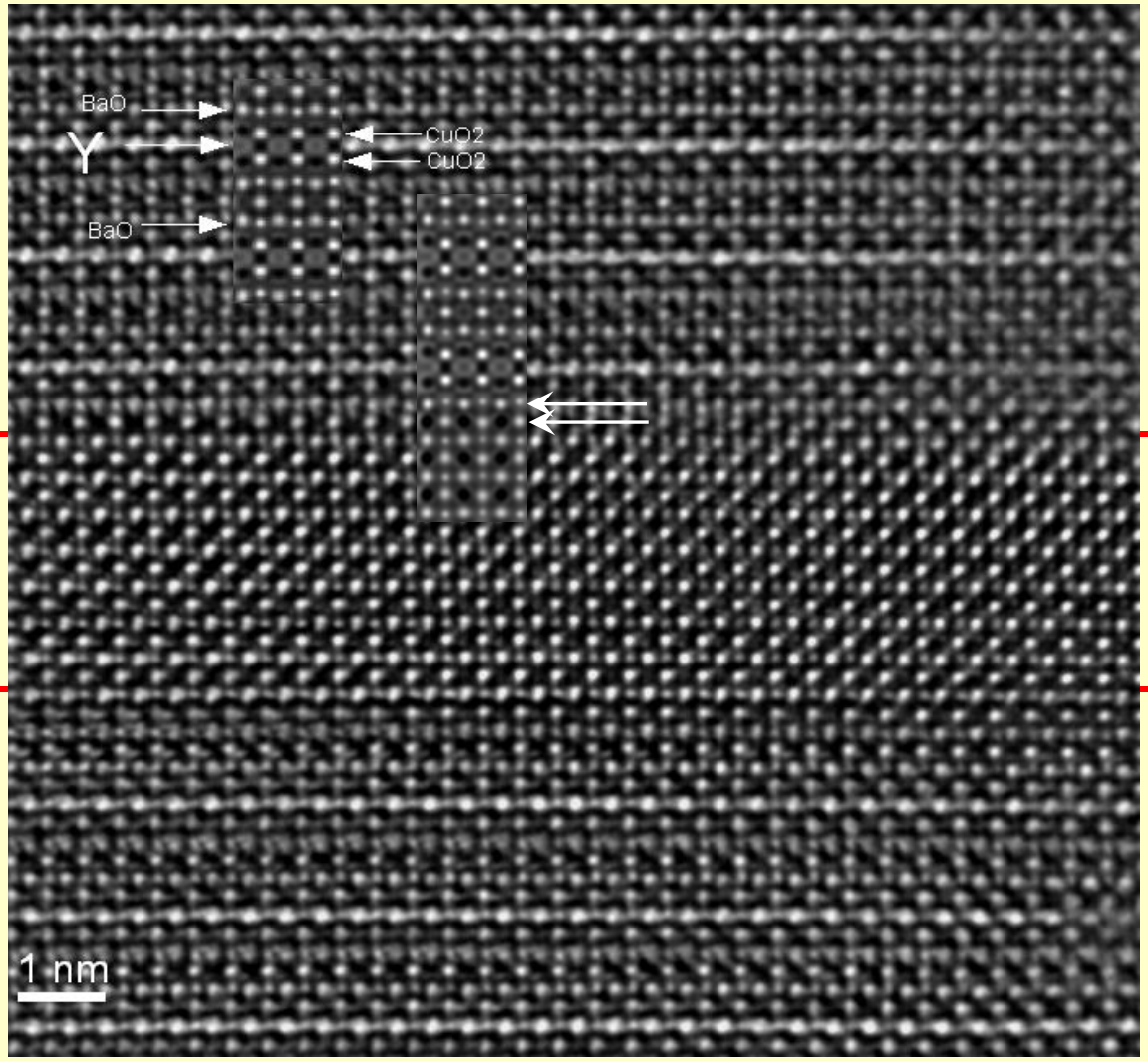
$YBaCu_2O_{7-x}$





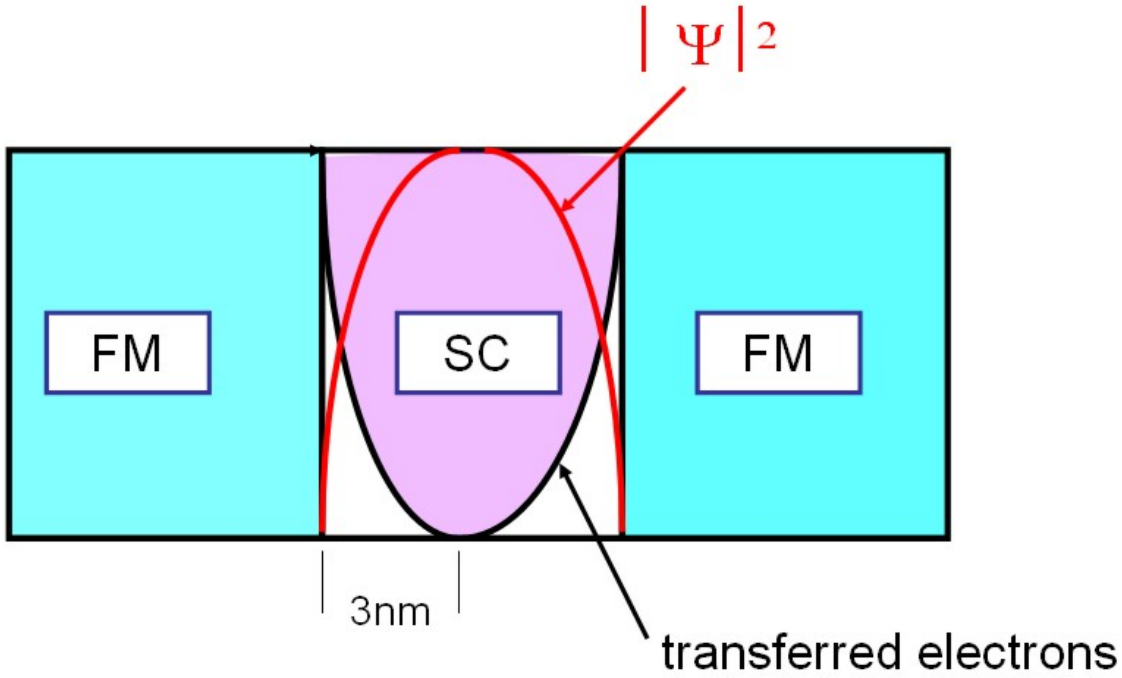
IS THAT THE WHOLE STORY ???

HRTEM (50nm YBCO / 3nm LCMO / 50 nm YBCO



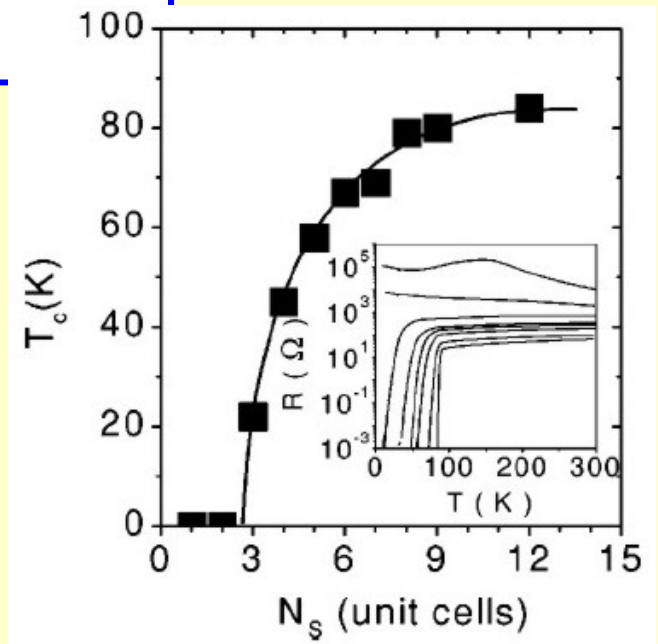
$T_C = 83$ K

$T^{Curie} =$ 210 K !!!!



“bulk“ T_c expected for t_{YBCO} > 6nm
~ 5 uc‘s

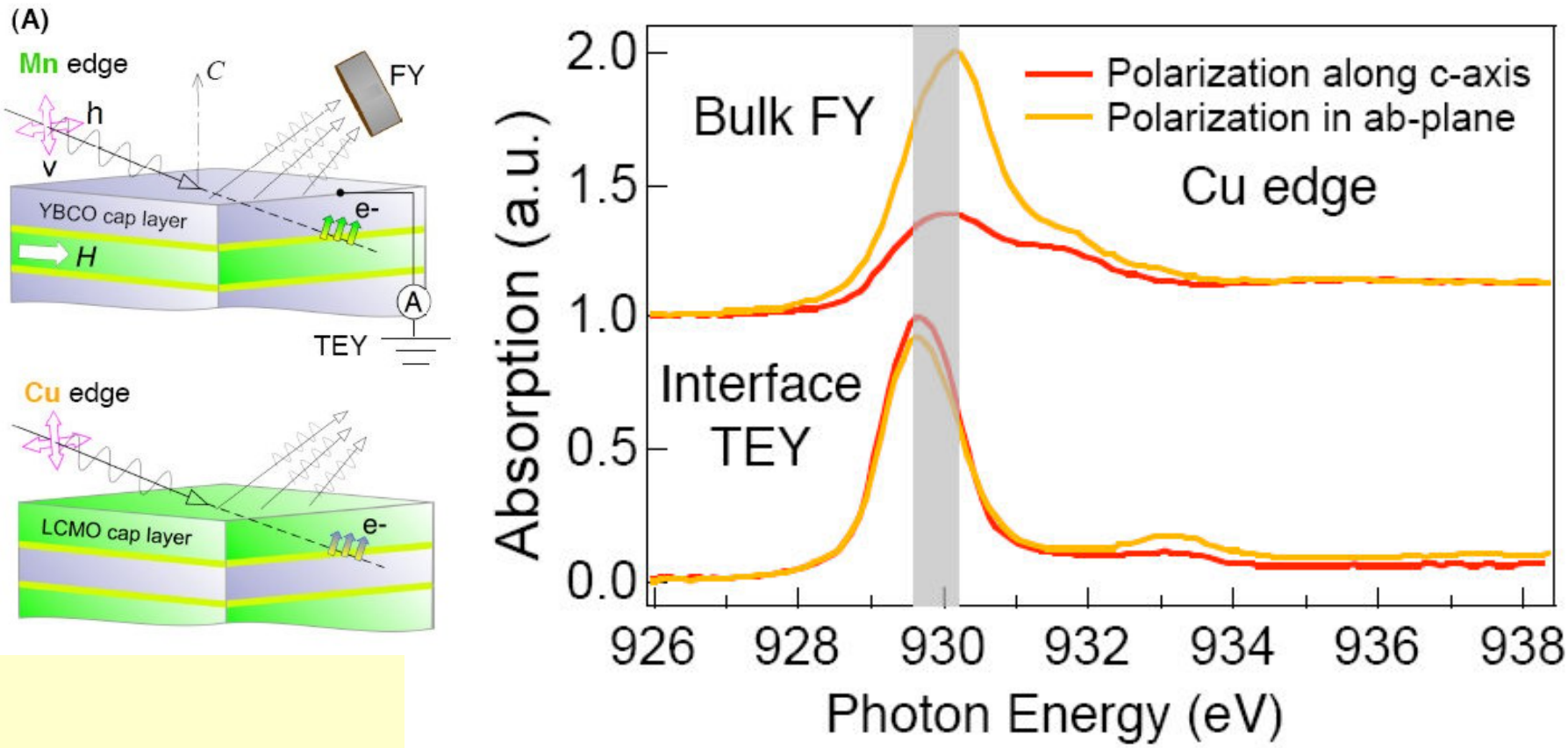
Sefrioui PRB 2003

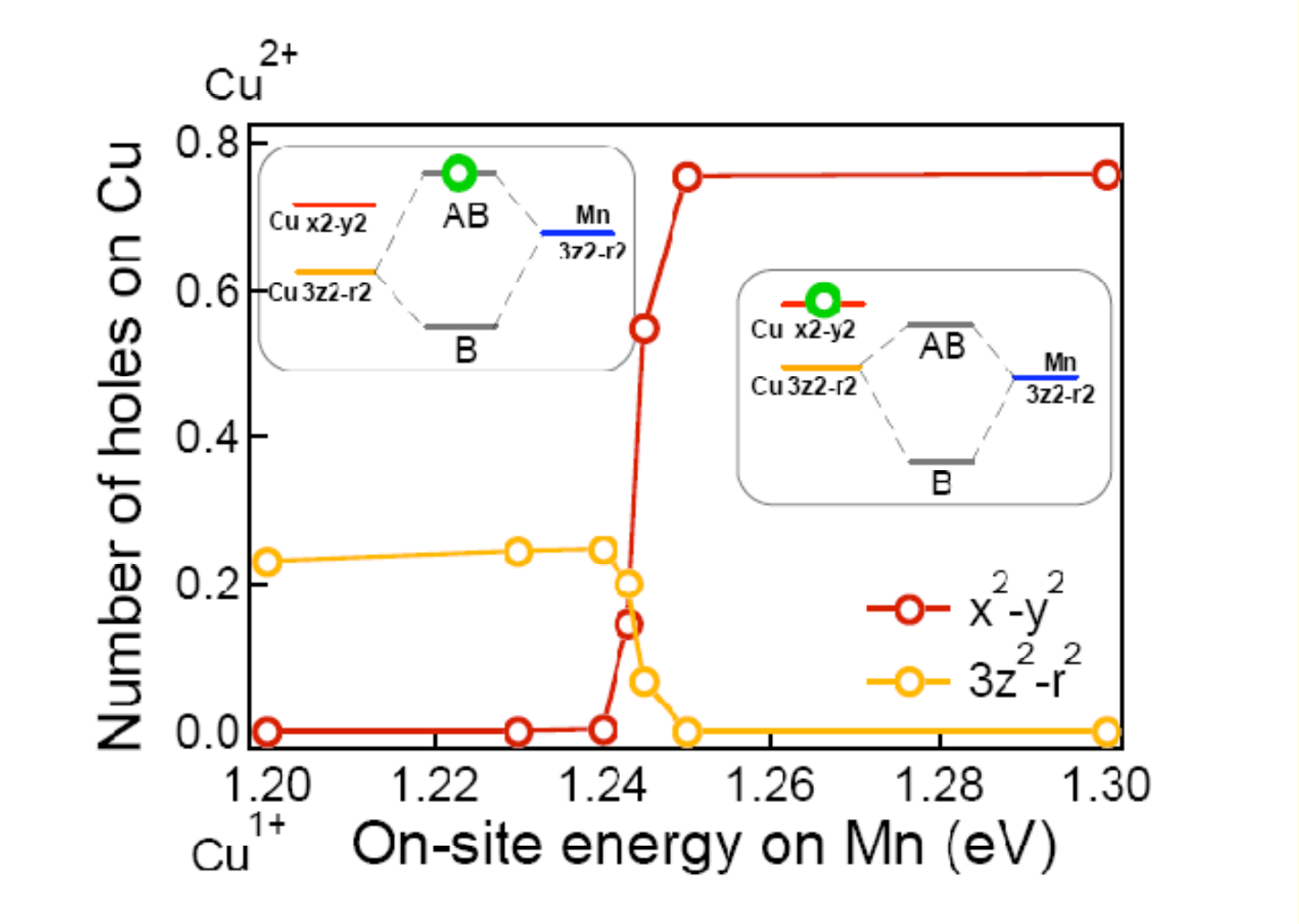


POLARIZED RESONANT X-RAY ABSORPTION

Recent results Chakhalian, Freeland, HUH,Keimer, Khaliullin

Science ***318*** *(2007) 1114*

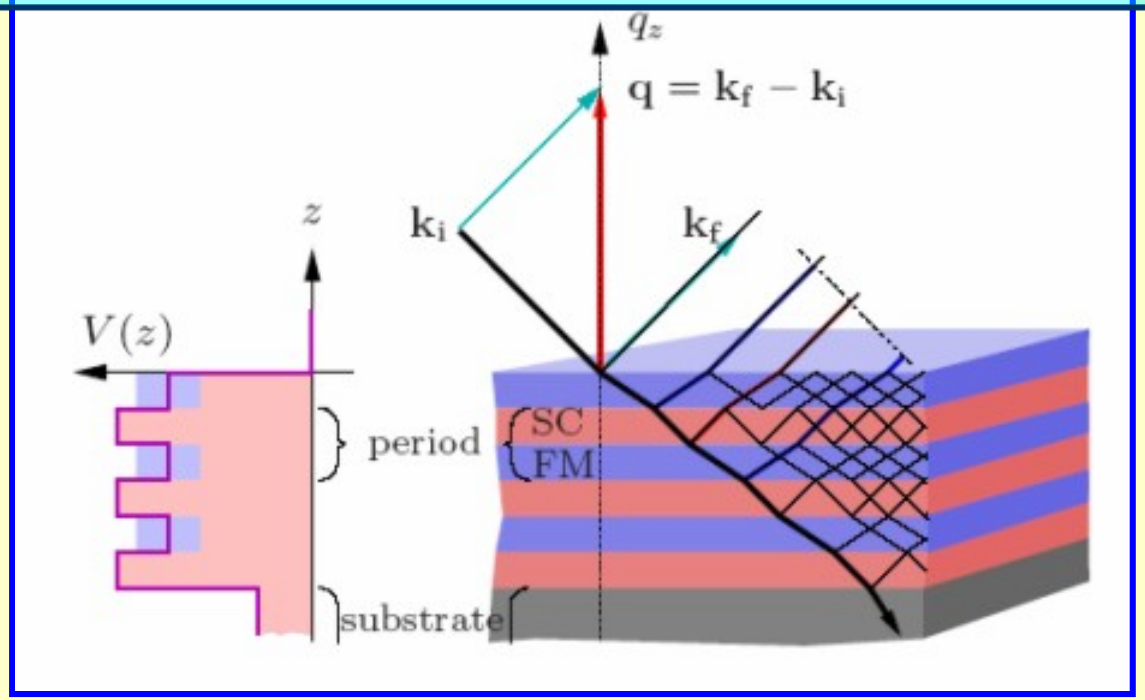


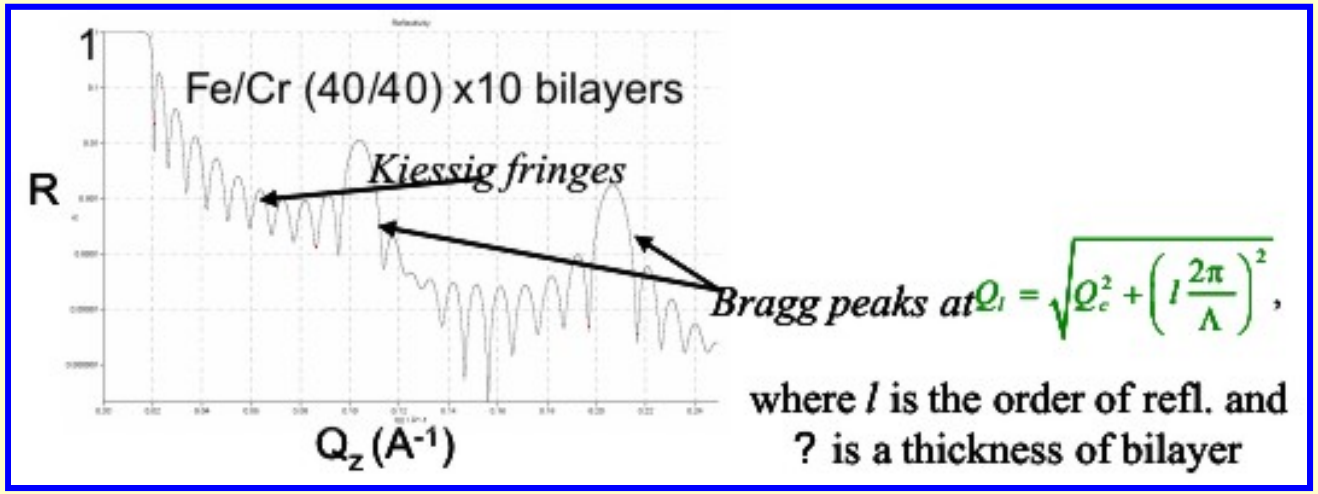


Occupancy of Cu d-orbitals at the LCMO-YBCO interface as a function of Mn hole on-site energy, as predicted by the exact diagonalization calculations.

J. Chakhalian ,J.W. Freeland, H.-U. H., G. Cristiani,G. Khaliullin, M. van Veenendaal, and B. Keimer Science 2007

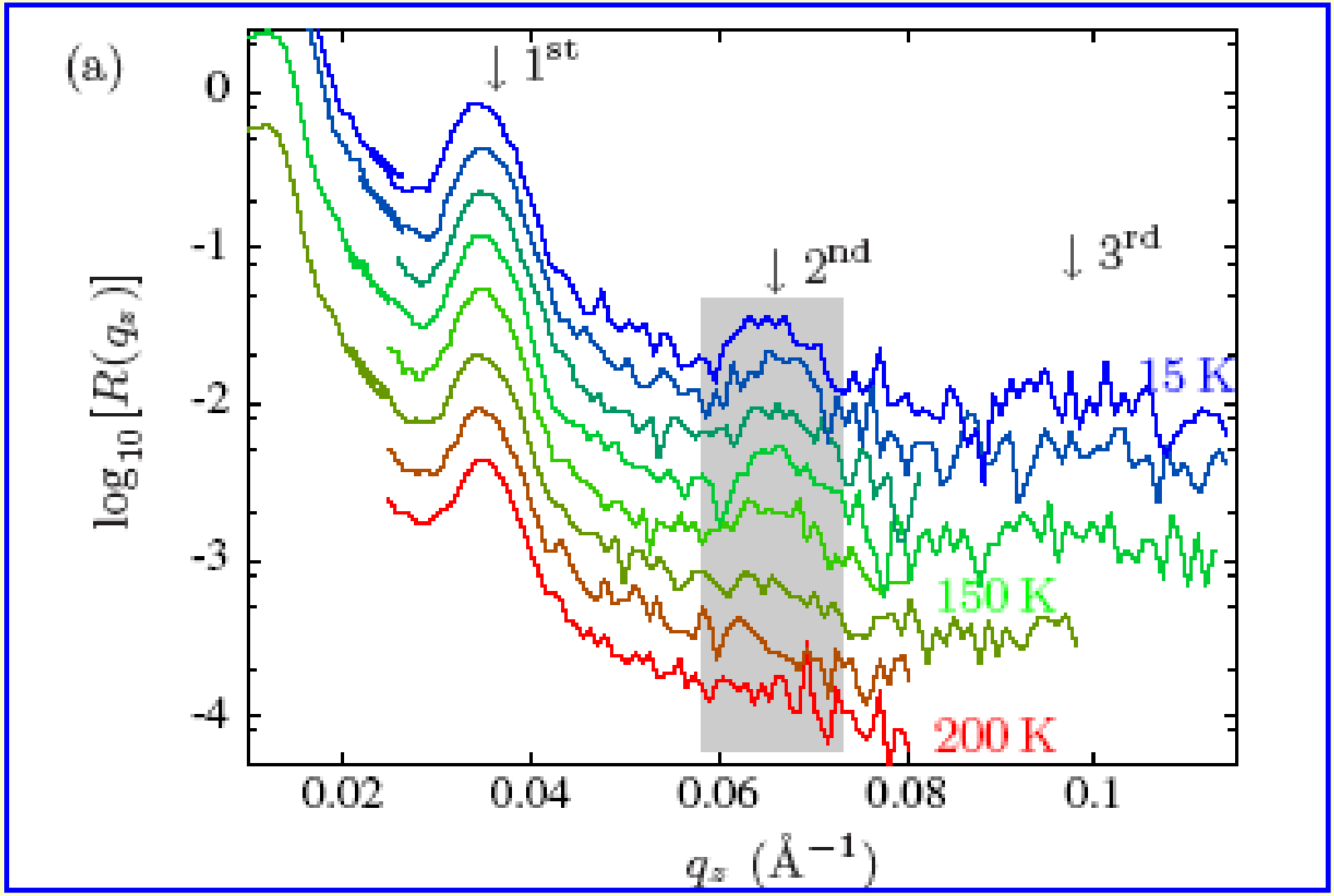
MAGNETIC CORRELATIONS AT INTERFACE AS REVEALED BY NEUTRON REFLECTOMETRY





specular neutron reflectivity

→ Bragg reflections due to structural and magnetic periodicity

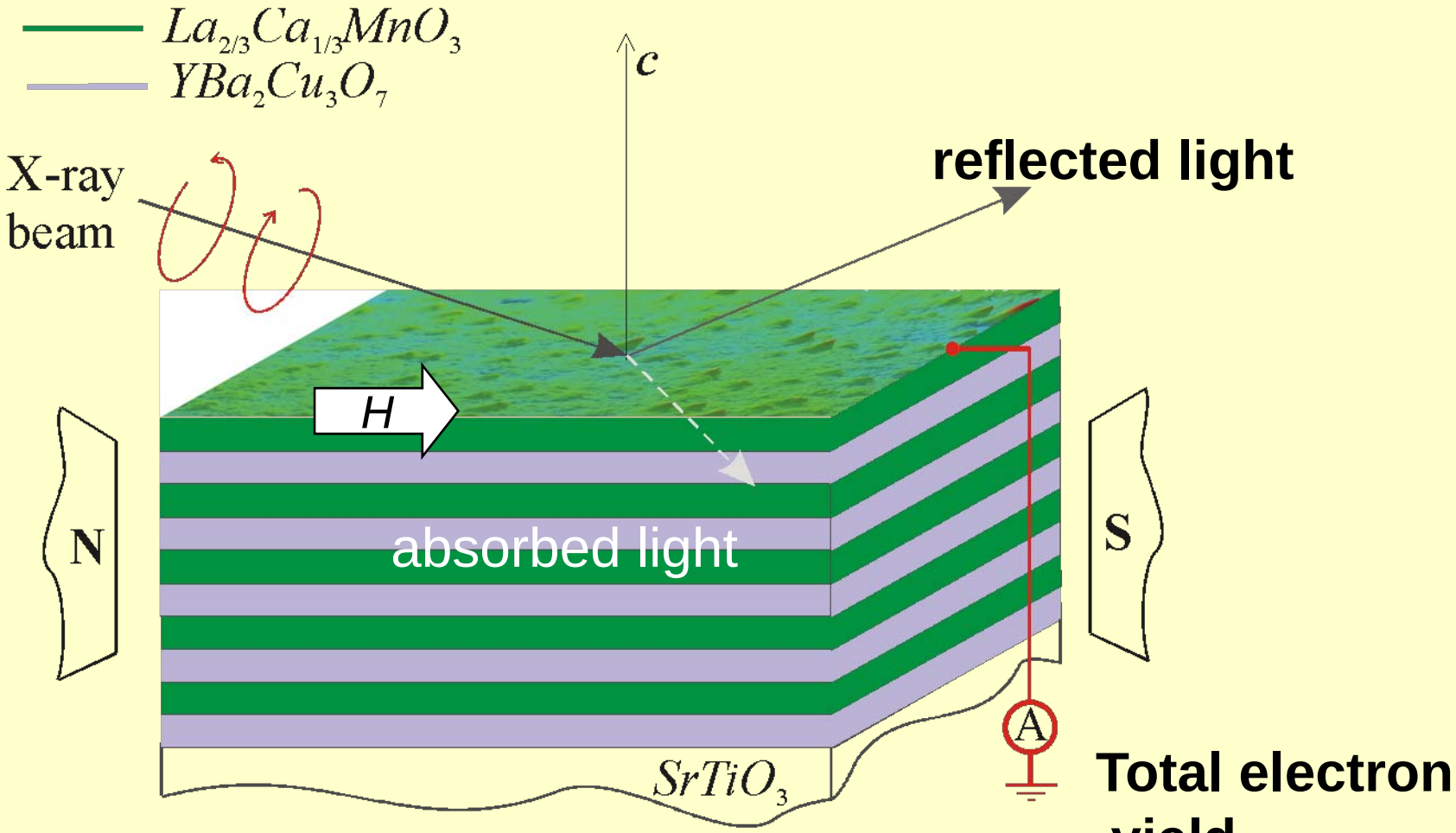


J. Stahn et al. Phys. Rev. B 71 (05) 140509 R

second Bragg peak forbidden if structural and magnetic denisty profiles are equal

Resonant soft X-ray absorption (XAS)

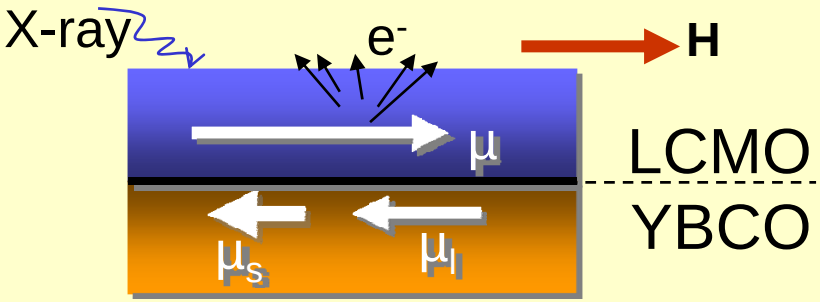
ELEMENT SPECIFIC PROBE OF MAGNETIC MOMENT

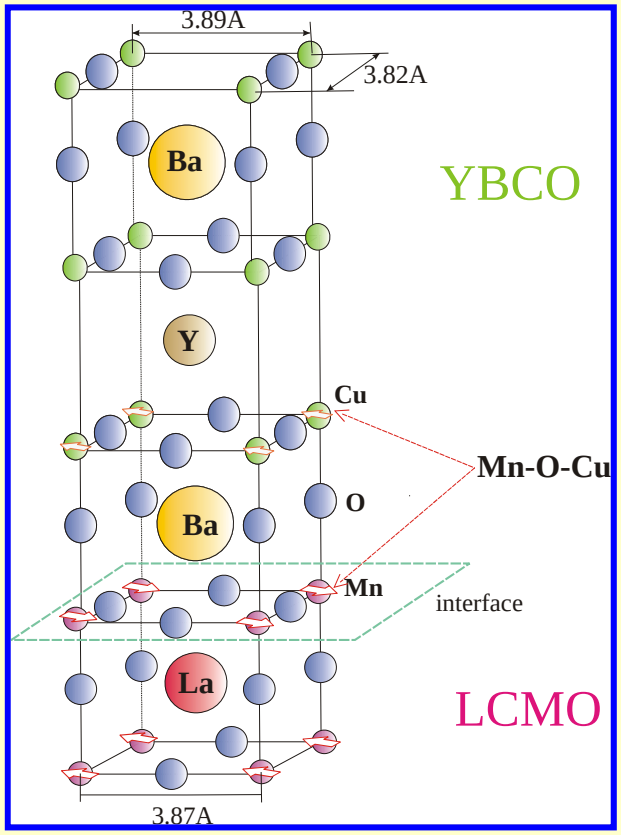


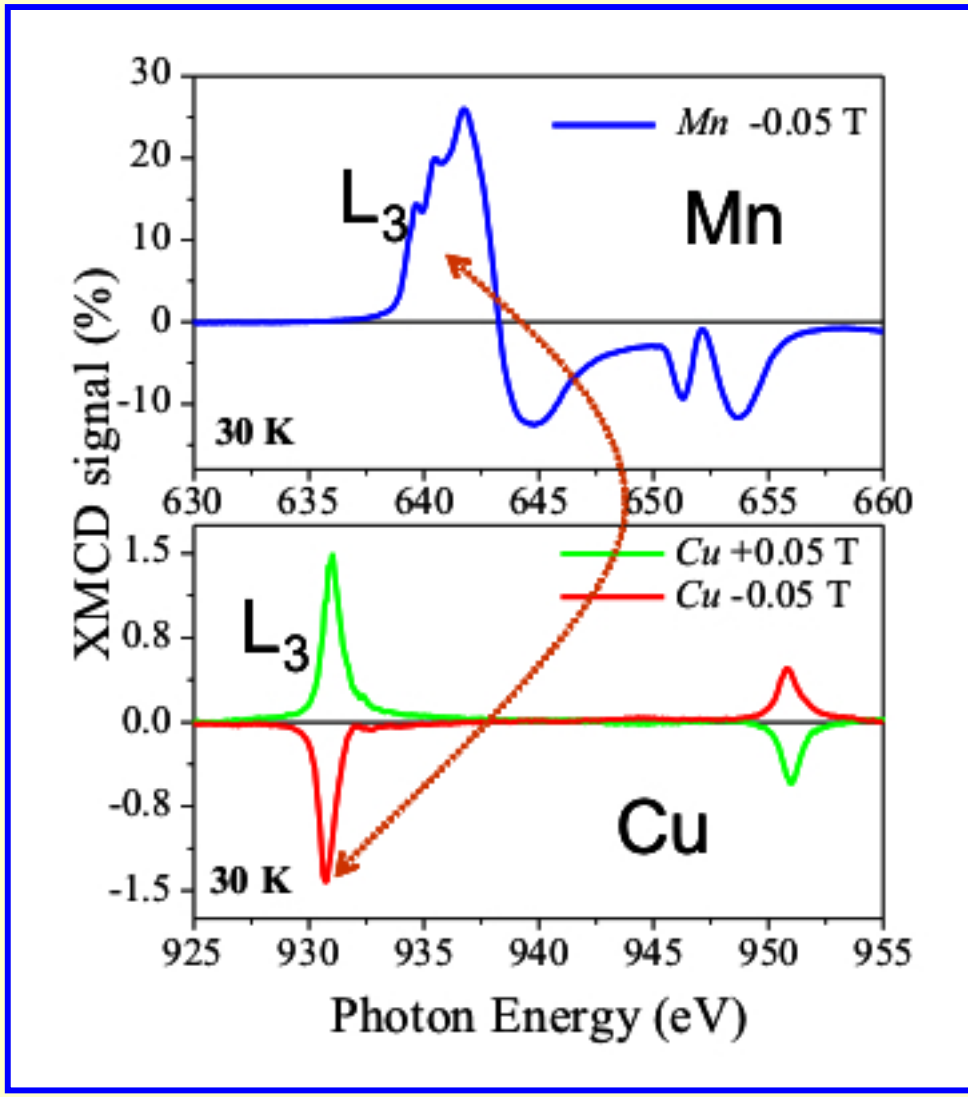
Soft x-ray range -100 eV -1.5 KeV
(3d generation facilities - **ESRF, APS, ALS**, SLS and CLS)

J. Chakhalian ,J.W. Freeland, H.-U. H., G. Christiani,G. Khaliullin, Ch. Bernhard, and B. Keimer Nature Physics 2 (2006) 244

X-ray magnetic dichroism in YBCO/LCMO SL

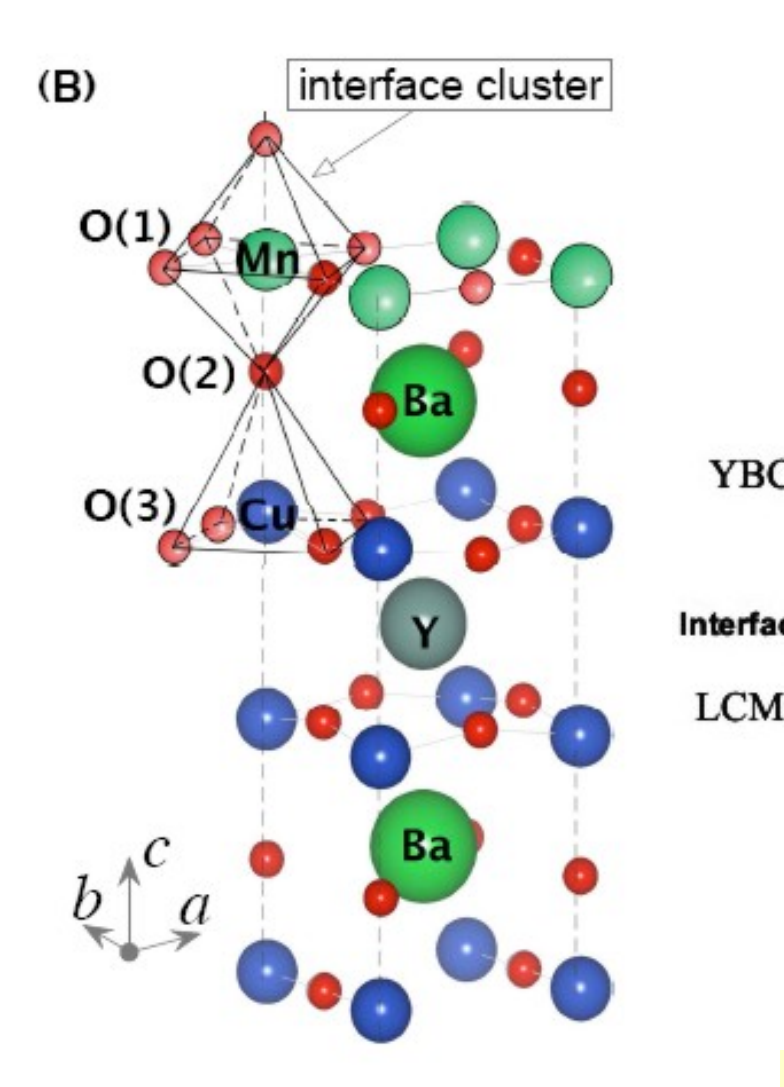


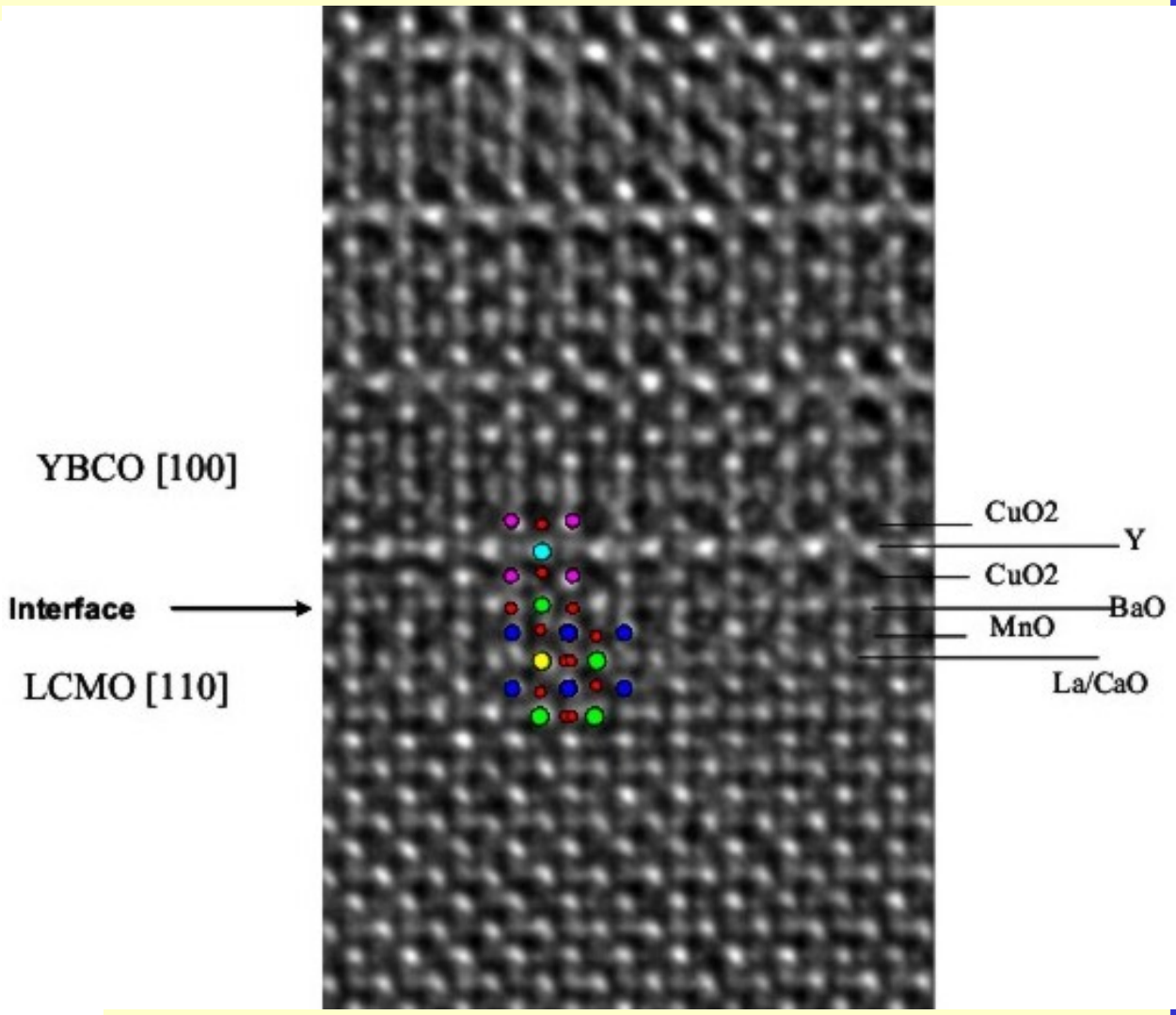




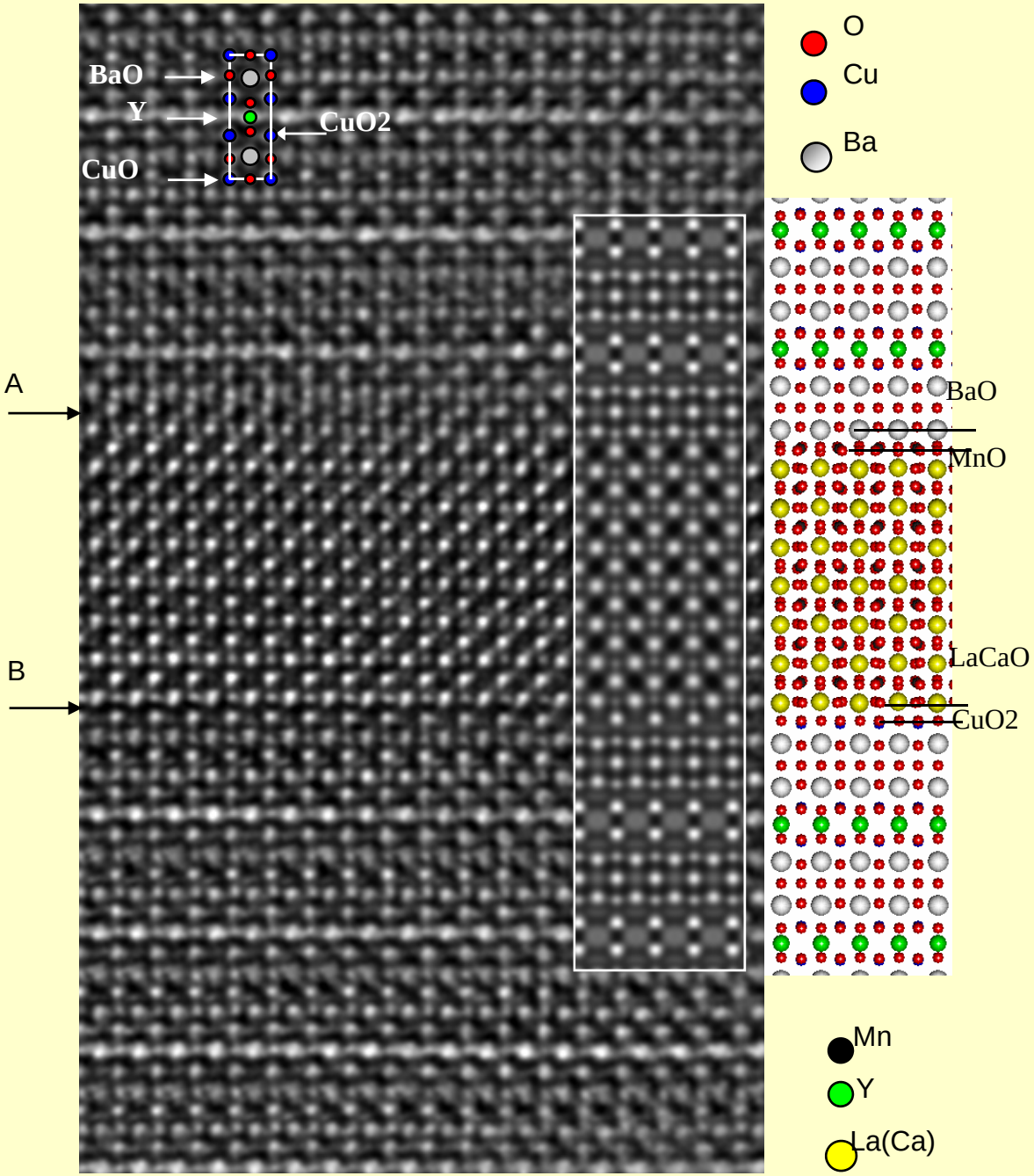
- **Magnetic moment on Cu below T_{sc} !**
- **Cu and Mn magnetic moments are *anti*-aligned.**

MODEL vs. REALITY





U. Kaiser + Z Zhang Uni Ulm Okt 2007



MIRROR INTERFACES

A - B vs B – A

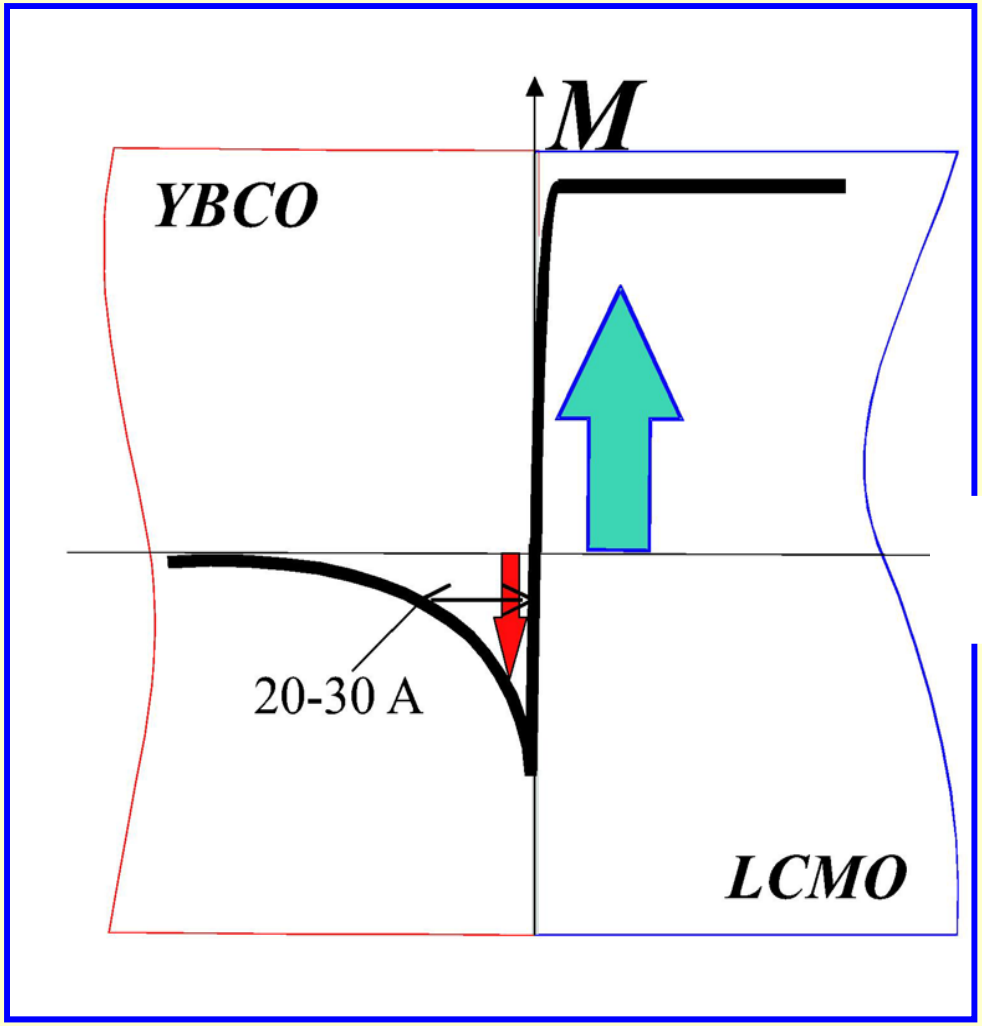
ARE NOT IDENTICAL

But

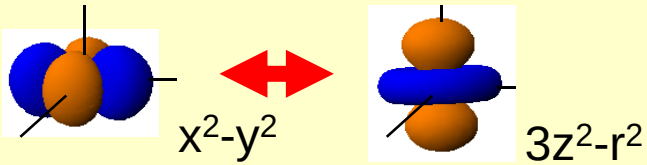
BOTH INCLUDE CuO_2

PLANES

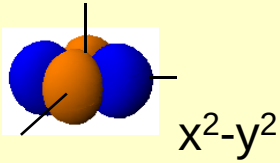
magnetization profile



assume bulk orbital occupancy is maintained at interface



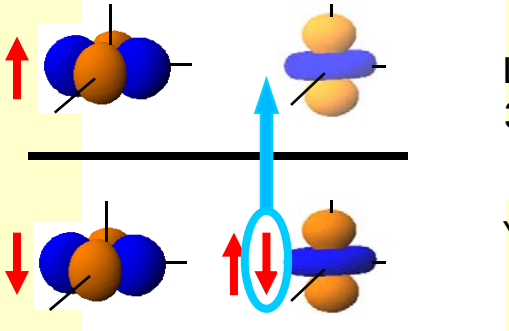
metallic LCMO: fluctuating orbital occupancy



metallic YBCO: x^2-y^2 orbital occupied

→*ferromagnetic* exchange coupling across interface inconsistent with experiment

orbital reconstruction at interface

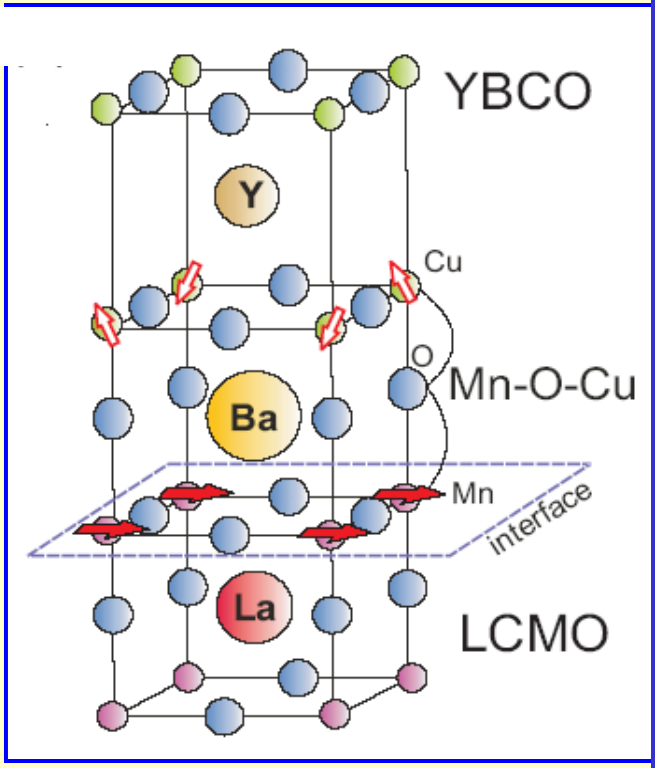


LCMO:
$3z^2$-r^2 orbital depleted

YBCO:

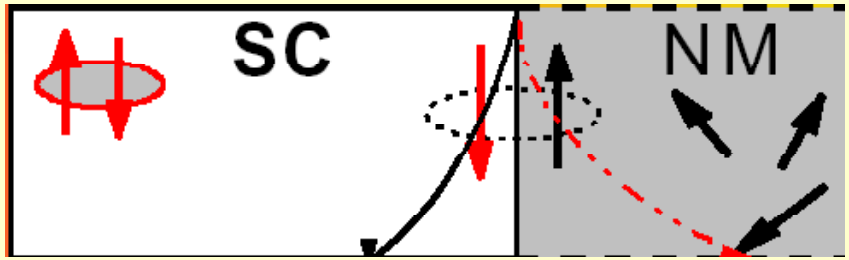
Superexchange interaction across interface

→ *antiferromagnetic* coupling, as observed

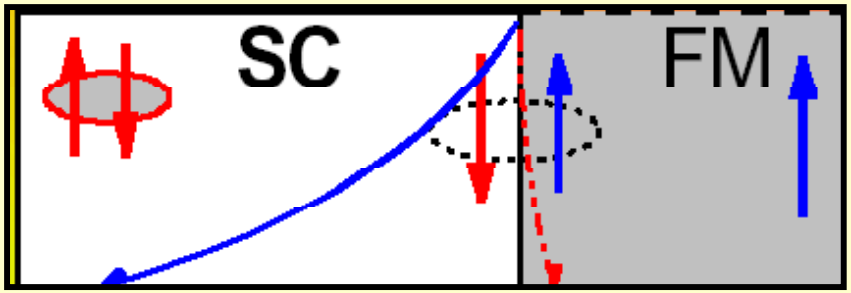


J.Chakhalian, J. Freeland, H.-U. H. et al. Nature Physics 2(2006) 244

INTERFACE PROPERTIES DOMINATE "BULK" PROPERTIES



$$\zeta_{NM} = (D_{NM} / 2 \pi T)^{1/2}$$

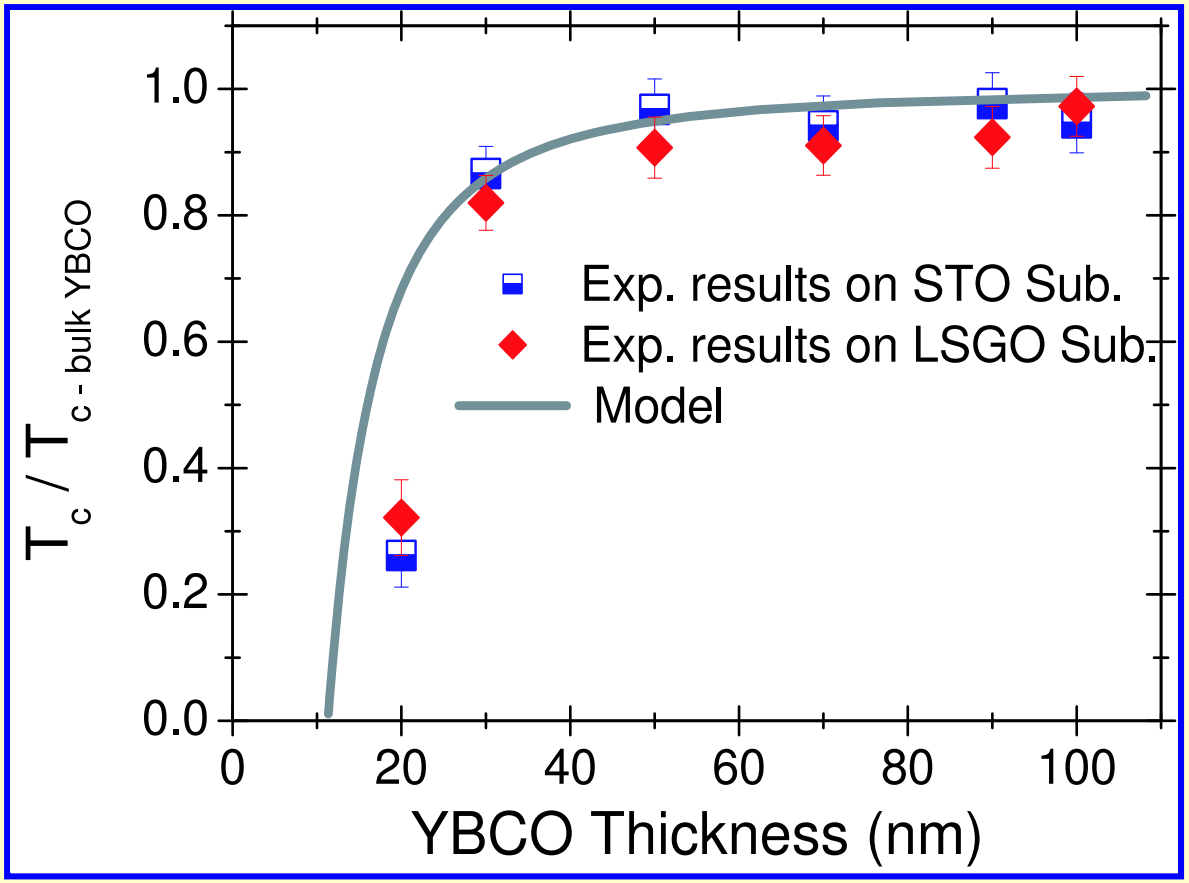


$$\zeta_{FM} = (D_{FM} / J)^{1/2}$$

SELF - INJECTION FROM FM SIDE

$$\Delta_{qp}/\Delta(0) = 1 - 2n_{qp} / 4N(0)\,\Delta(0)$$

$$d = \alpha \xi_{FM} \cong 3.7 \frac{\alpha m^* \hbar v_F^2}{\Delta(0) \Delta E_{ex} n_{qp}(0) e^2} \frac{\sqrt{T/n_{qp}(T)}}{\sqrt[4]{1-(T/T_c)}}$$

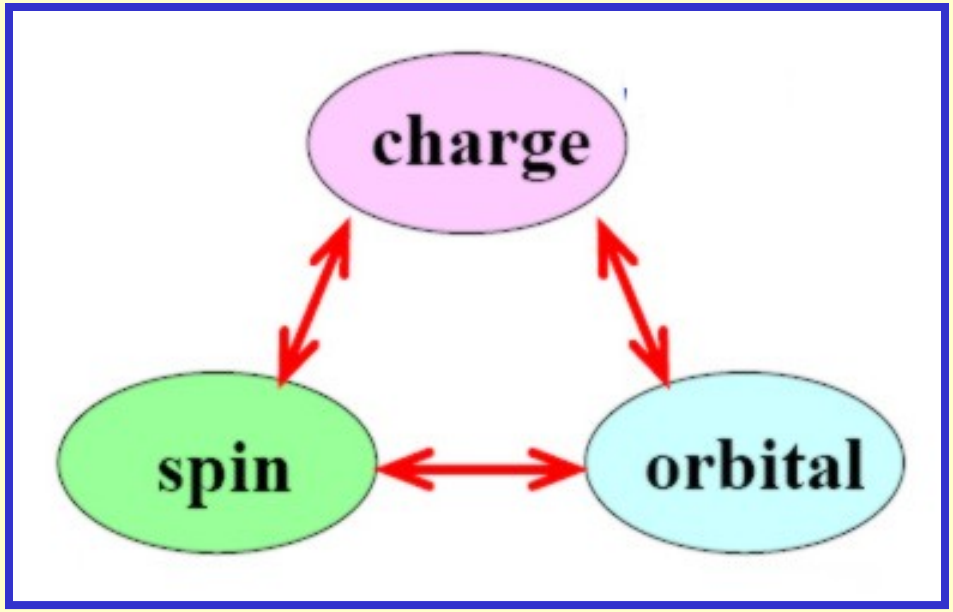


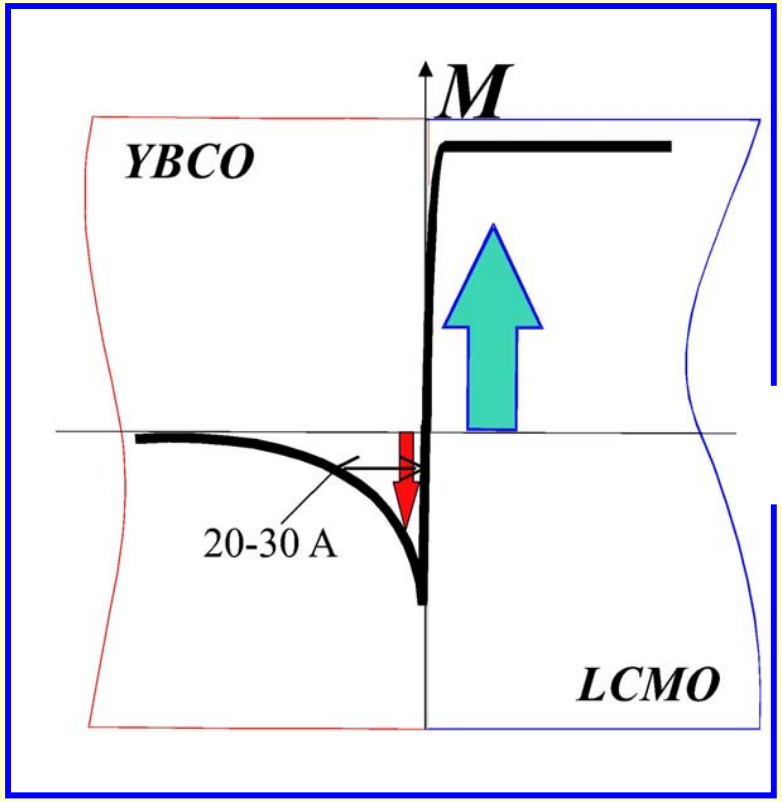
S. Soltan, J. Albrecht, H.-U.H. PRB 70 (2004) 144517

4. TOWARDS AN UNIFIED VIEW

nanoscopic short length scale < 3 nm

charge transfer **and**
orbital reconstruction





IS THAT THE WHOLE STORY ???

nanoscopic medium length scale 3 nm < x < 10nm

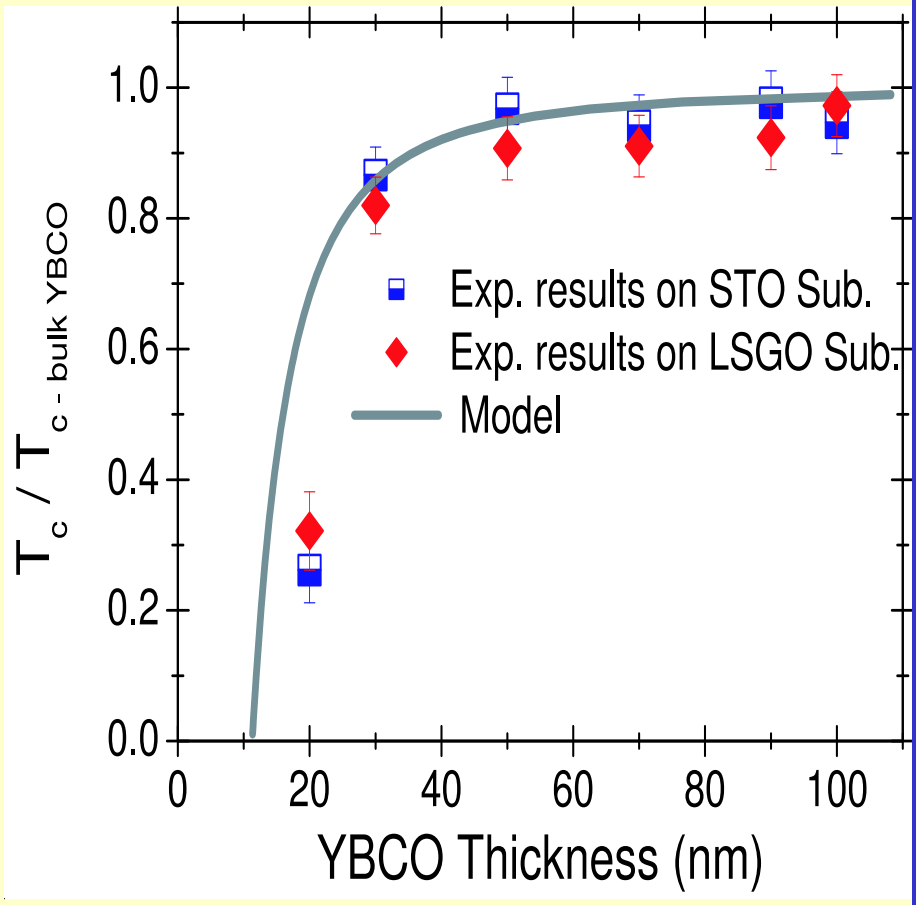
spin polarized quasiparticle diffusion

SPQ scattering center for

Cooper-pairs → T_c reduction

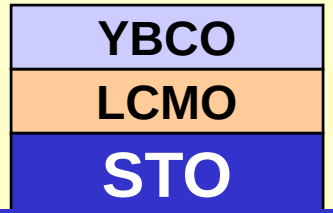
S.Soltan et al. PRB 70 (2004)

$$d \approx \alpha \xi_{fm} \approx 3.7 \frac{\alpha m^* \hbar^2 v_F}{\Delta(0) \Delta J_{spin} n_{qp}(0) e^2} \frac{\sqrt{T / n_{qp}(T)}}{\sqrt[4]{1-(T/T_c)}}$$



Strongly suppressed free charge carrier response for symm. SL with $\Lambda < 20$nm

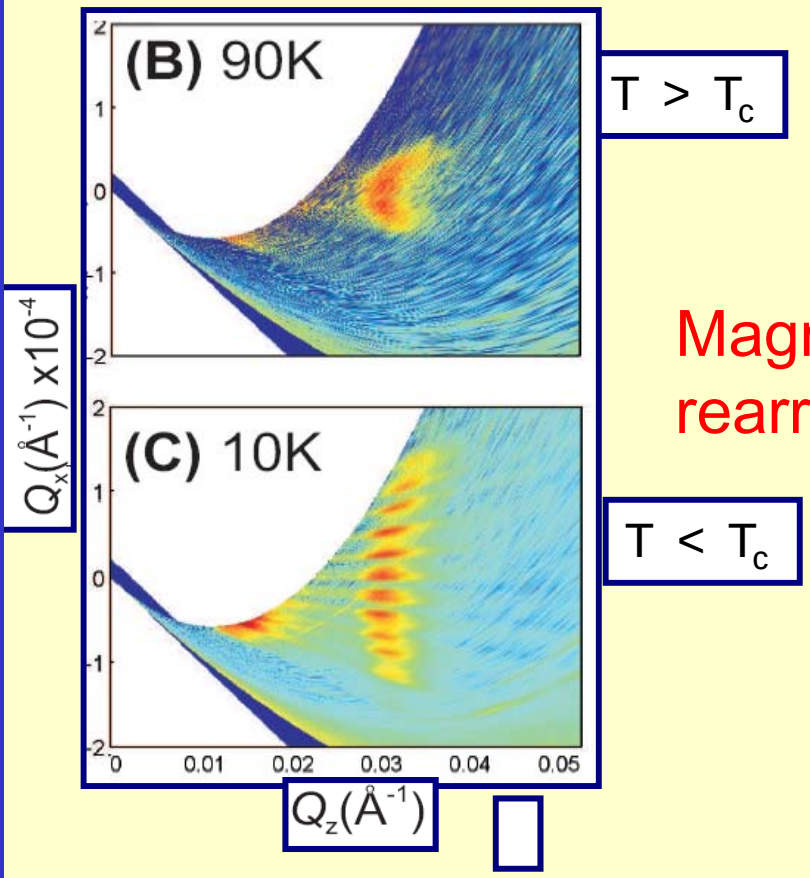
T. Holden *et al.,* Phys. Rev. B 69, (2004) 064505



mesoscopic length scale > 10nm

effects dominated by magnetic interactions

off specular neutron reflectivity

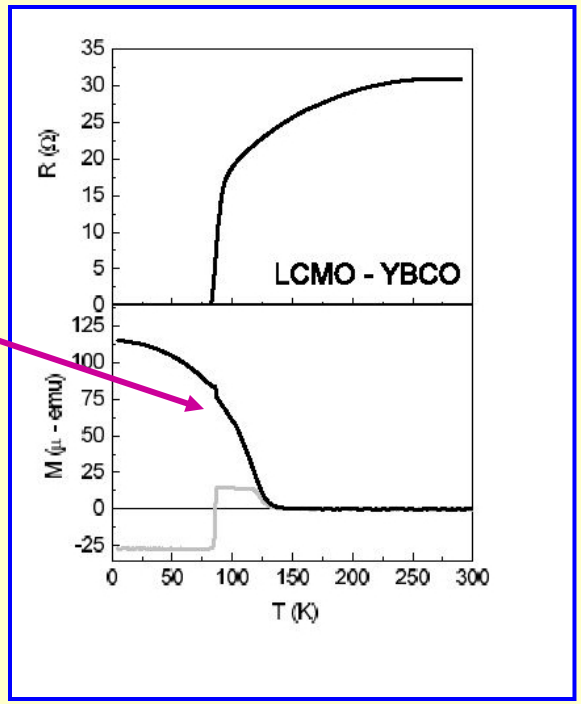


$T > T_c$

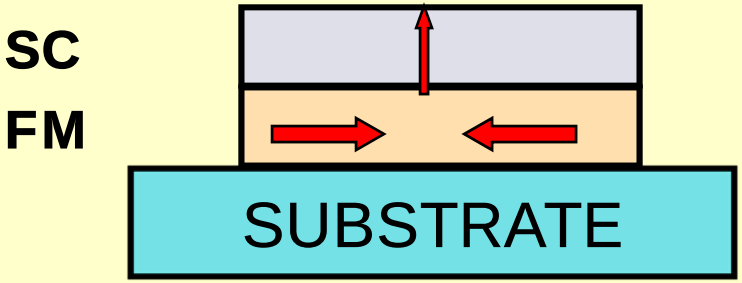
$T < T_c$

Jump in FC- M(T)

@ T_c



Magnetic domain rearrangement @ T_c



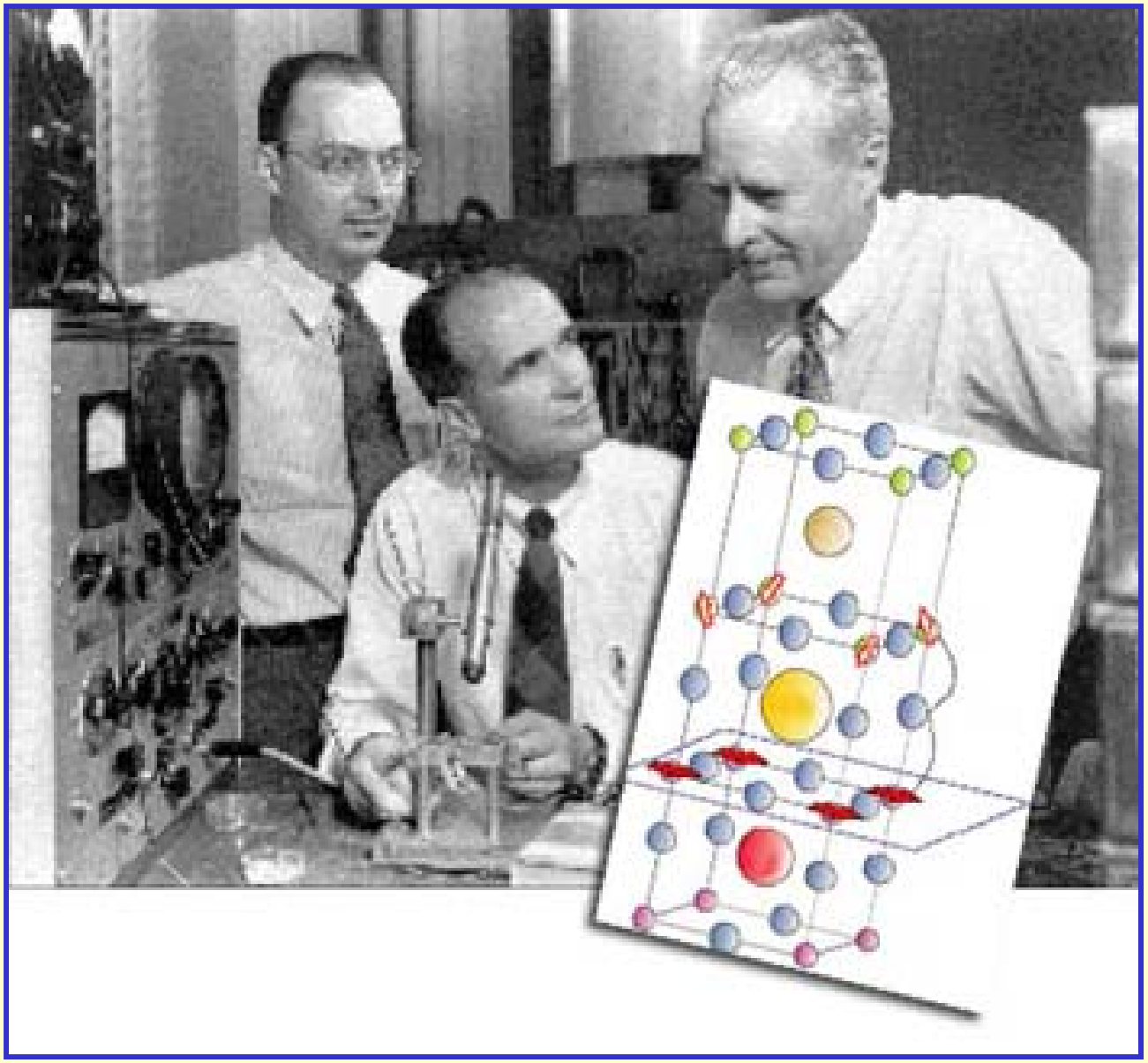
new superstructure

below T_C periodicity ~ 1μm

Vortex physics different in HS's and SL's

5. CONCLUSIONS

1. IN YBCO-LCMO SUPERLATTICES THERE ARE INTERACTIONS AT DIFFERENT LENGTH SCALES ξ AT WORK
2. FOR $\xi < 3nm$ ORBITAL RECONSTRUCTION AND CHARGE TRANSFER EFFECTS DOMINATE
3. $3nm < \xi < 10nm$ IS THE REGIME FOR SPINDIFFUSION
4. MAGNETIC INTERACTIONS DOMINATE AT LENGTH SCALES IN THE SUB-μm RANGE



Web-page from Argonne National Lab

THANKS FOR YOUR ATTENTION

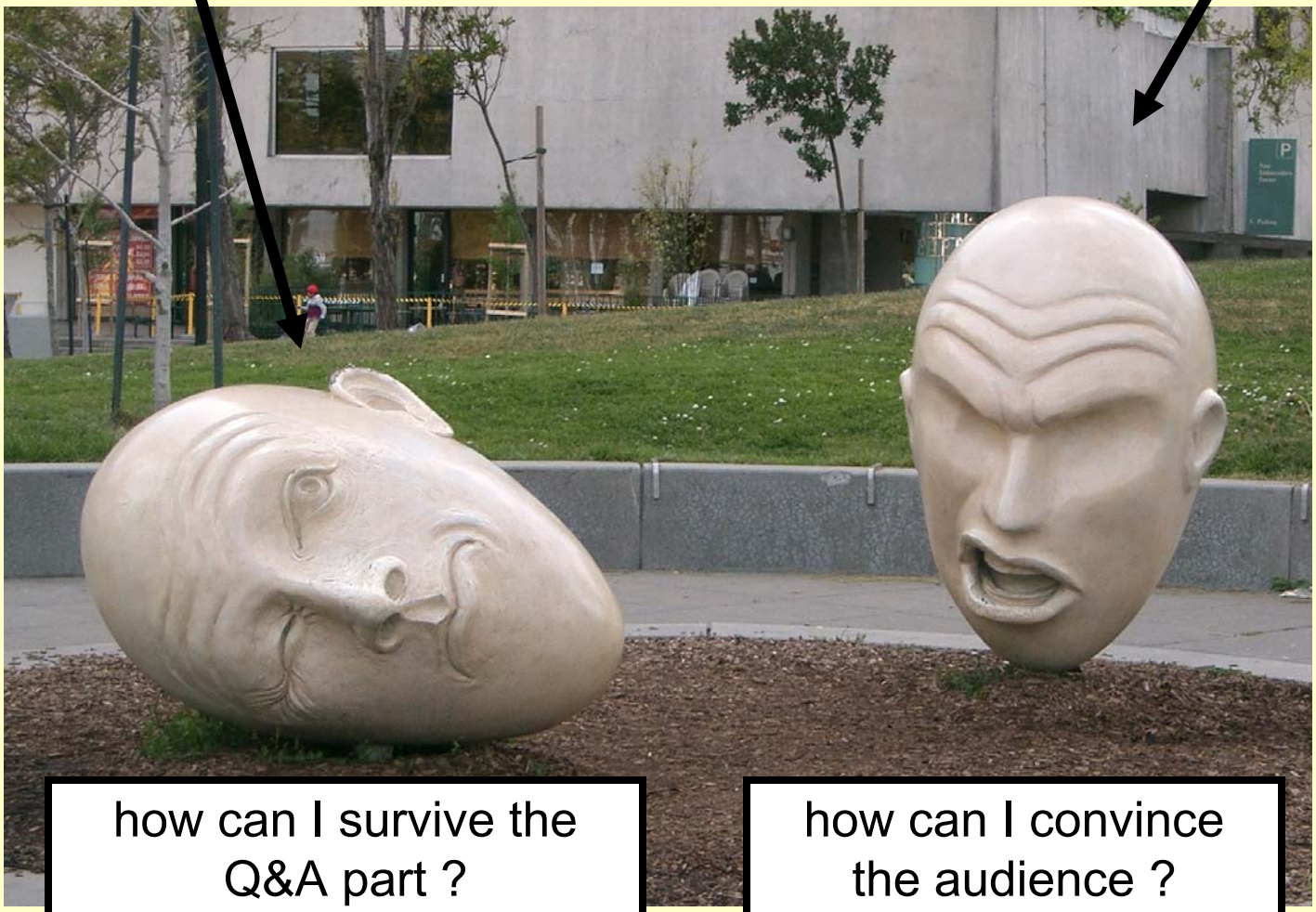
FROM THE BEGINNING

TO THE END

QUESTIONS COMMENTS CRITICISM ?

after the first question

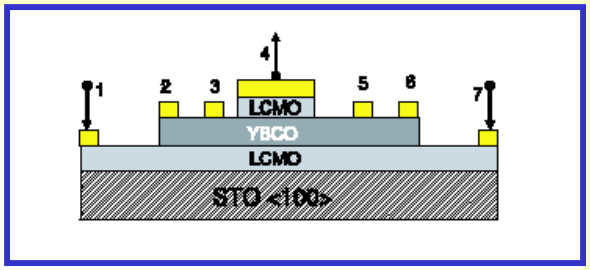
during the talk

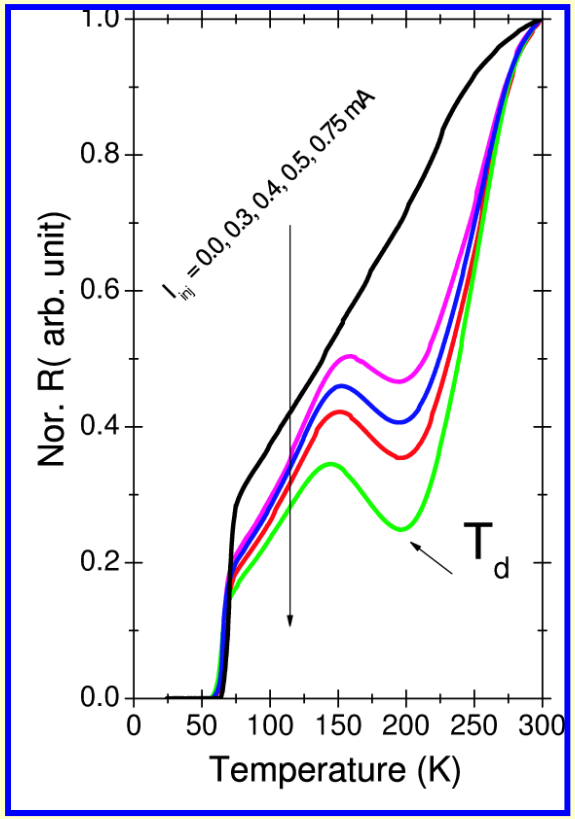


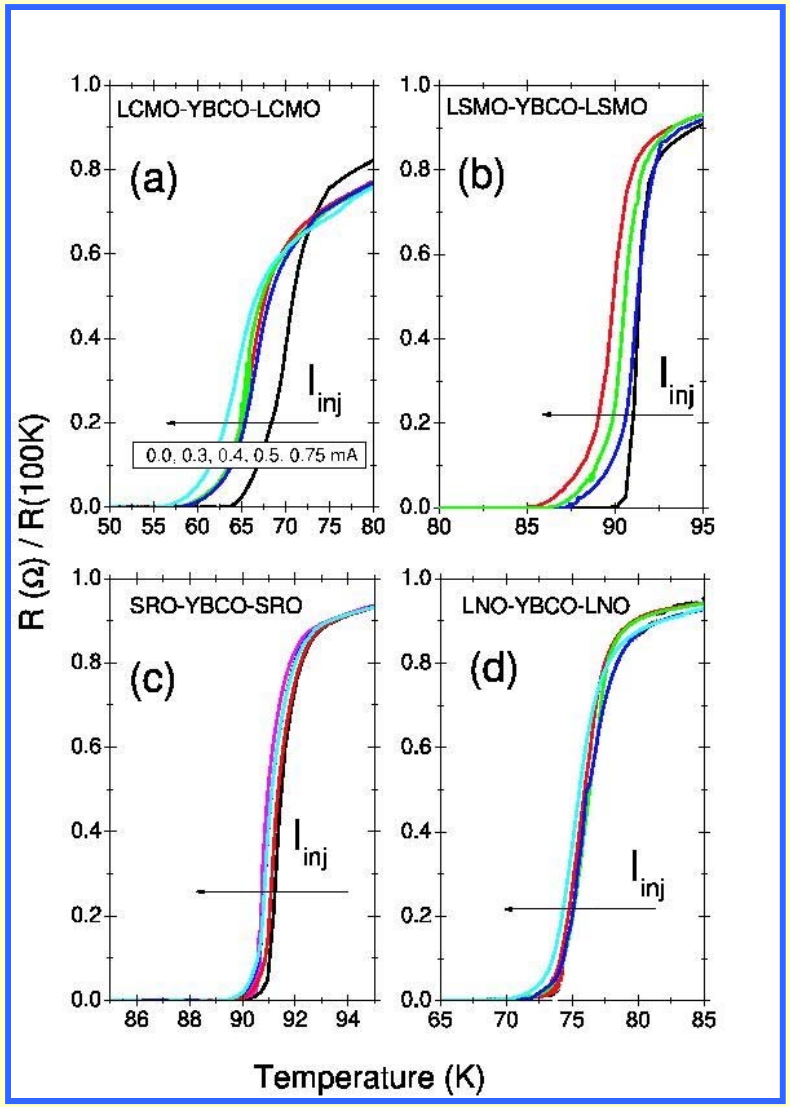
how can I survive the Q&A part ?

how can I convince the audience ?

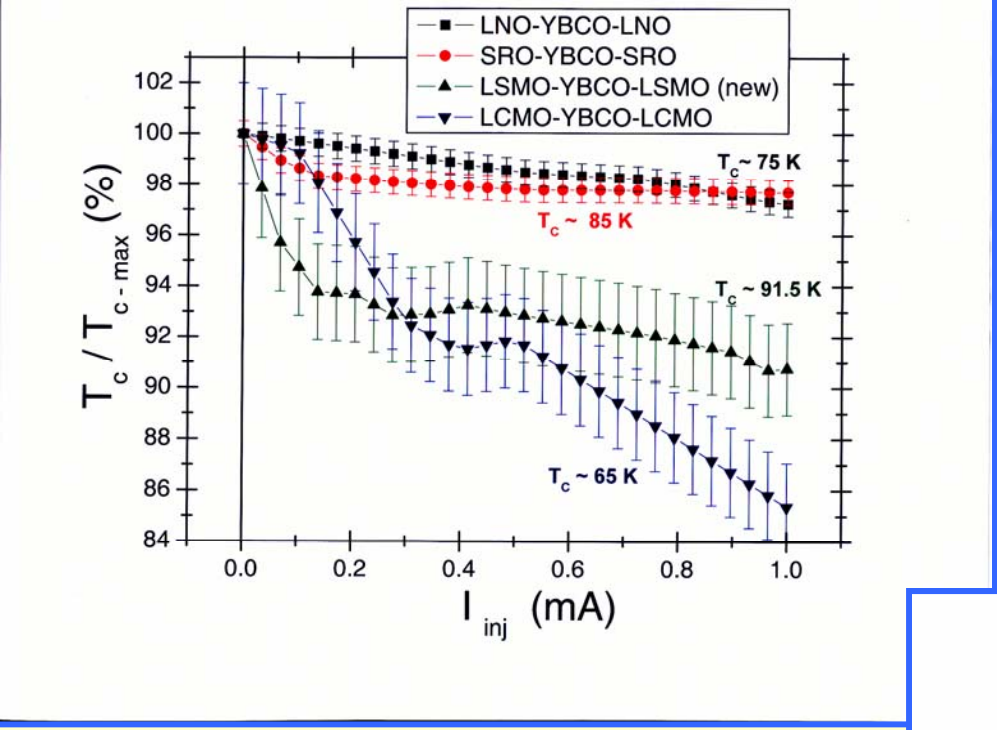
2. Spin-polarized quasiparticle injection into HTSC thin films
The role of the spin in cuprates





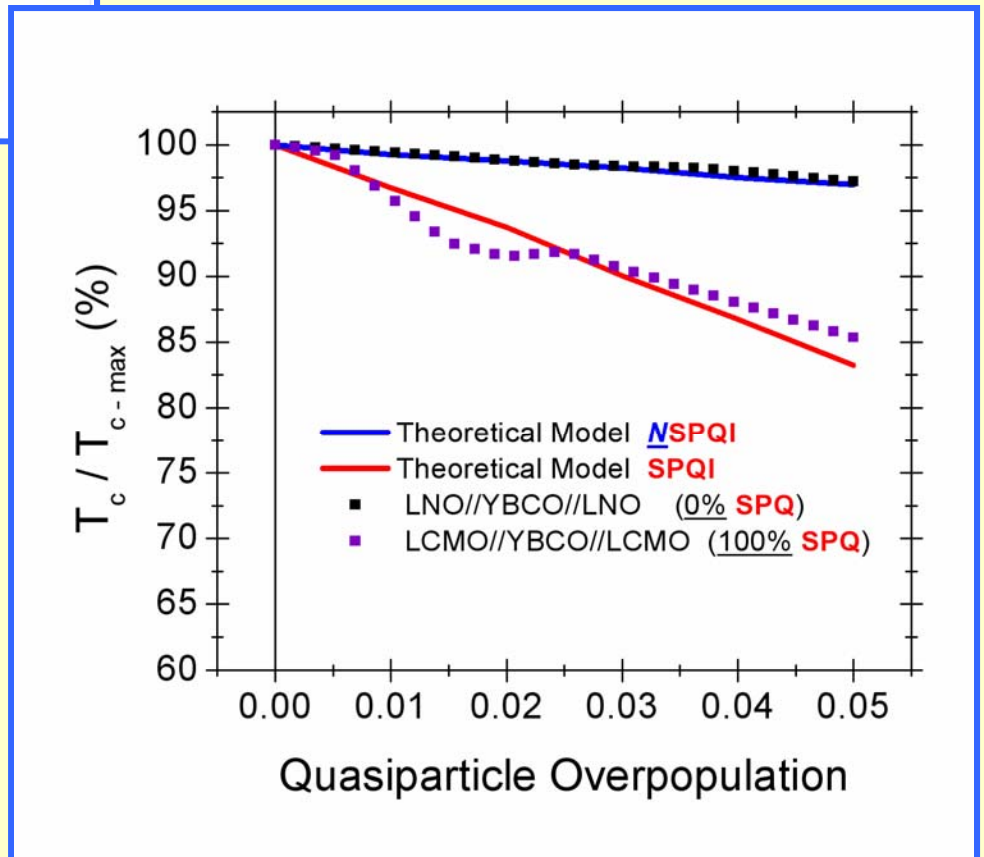


S.Soltan, J. Albrecht and H.-U. H. .Solid State Comm. **135** (2005) 461



SPIN MATTERS !!!

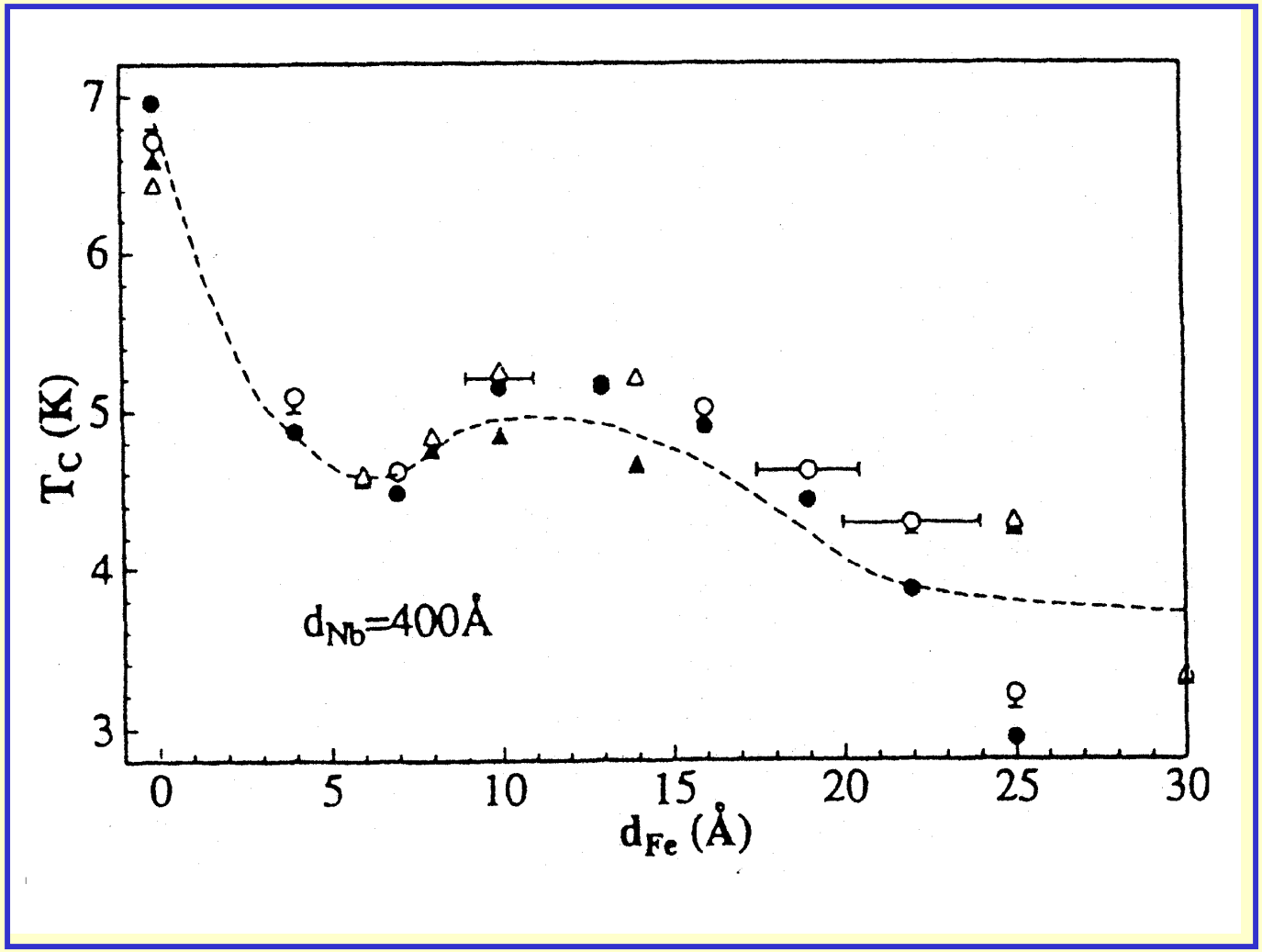
BHATTACHARJEE and SARDAR based on OWEN – SCALAPINO μ* model (excess QP's modified chem. potential)



2. Oscillatory Phenomena in Metallic FM / SC Hybrids

Larkin-Ovchinnikov-Fulde-Ferrel [LOFF] States

Mühge et al. PRL 77 (1996)1857



PHYSICALLY MEANINGFUL MODELS

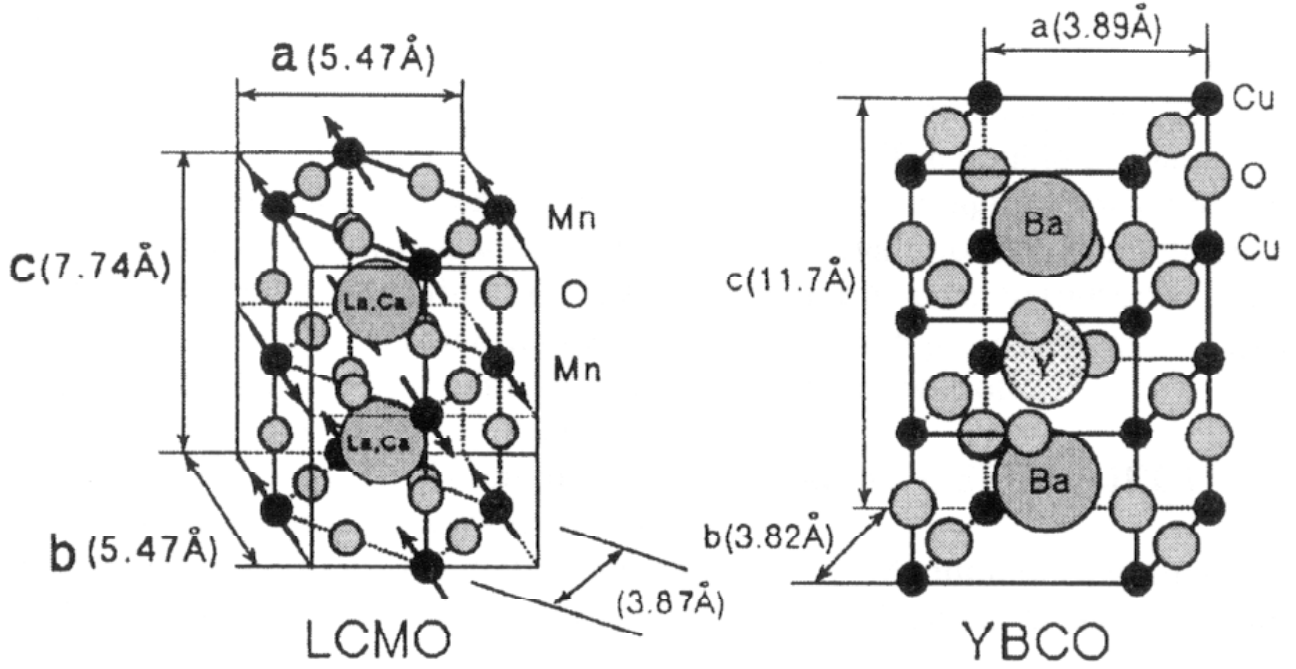
- **Antiferromagnetic coupling between the FM layers**

  ↷ **Doubled period - additional Bragg peaks at**
  q_z = 0.022 Å and q_z = 0.053 Å not observed

- **Magnetic roughness of any length scale**

  ↷ **Faster decay of reflectivity -**
  no 2nd Bragg peak appears

- **Conventional magnetic proximity effect**
  Exponential decay of magnetization in SC failure



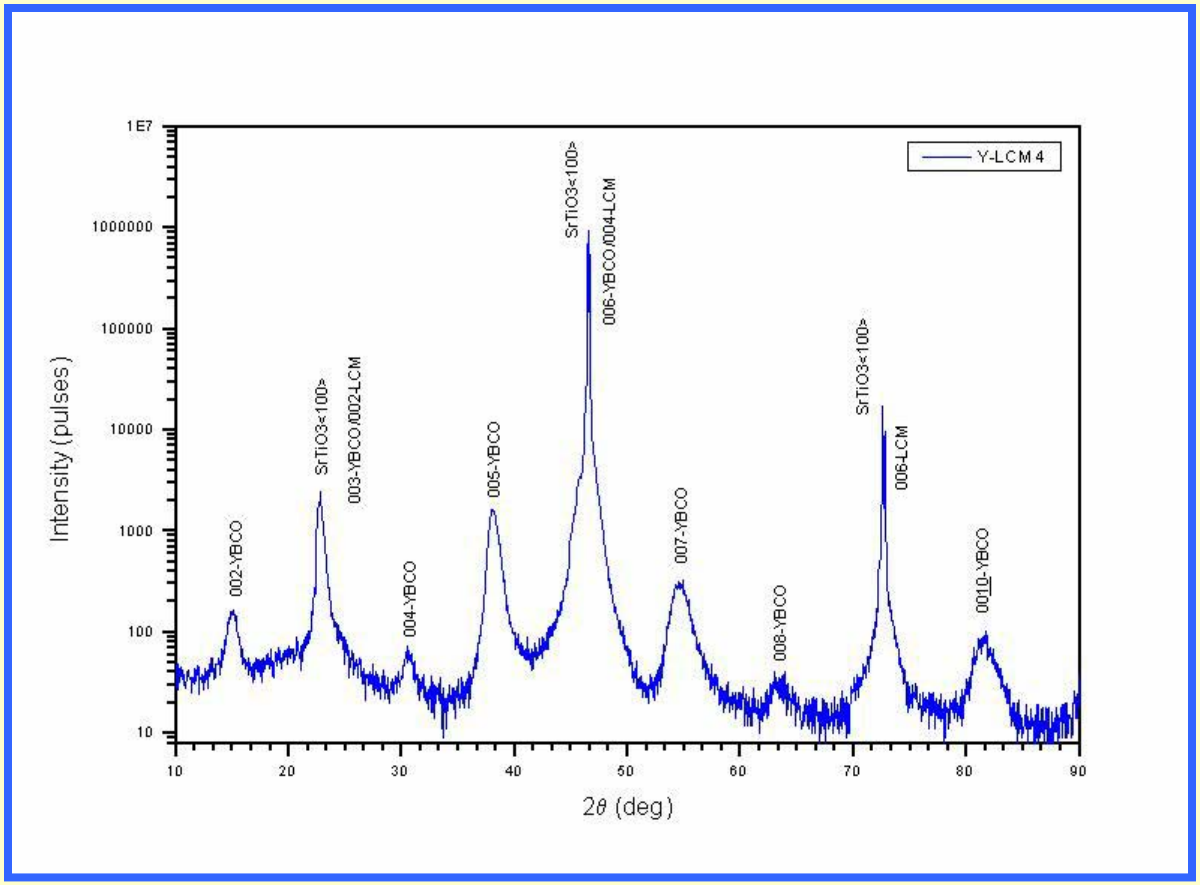
Unit cells of $YBa_2Cu_3O_7$ (YBCO) and $La_{2/3}Ca_{1/3}MnO_3$ (LCMO) showing various dimensions.

LATTICE MISMATCH

(no correction w.r.t. deposition temperature and different thermal expansion coefficients)

YBCO/LCMO: 0.38% YBCO /STO: 1.4%

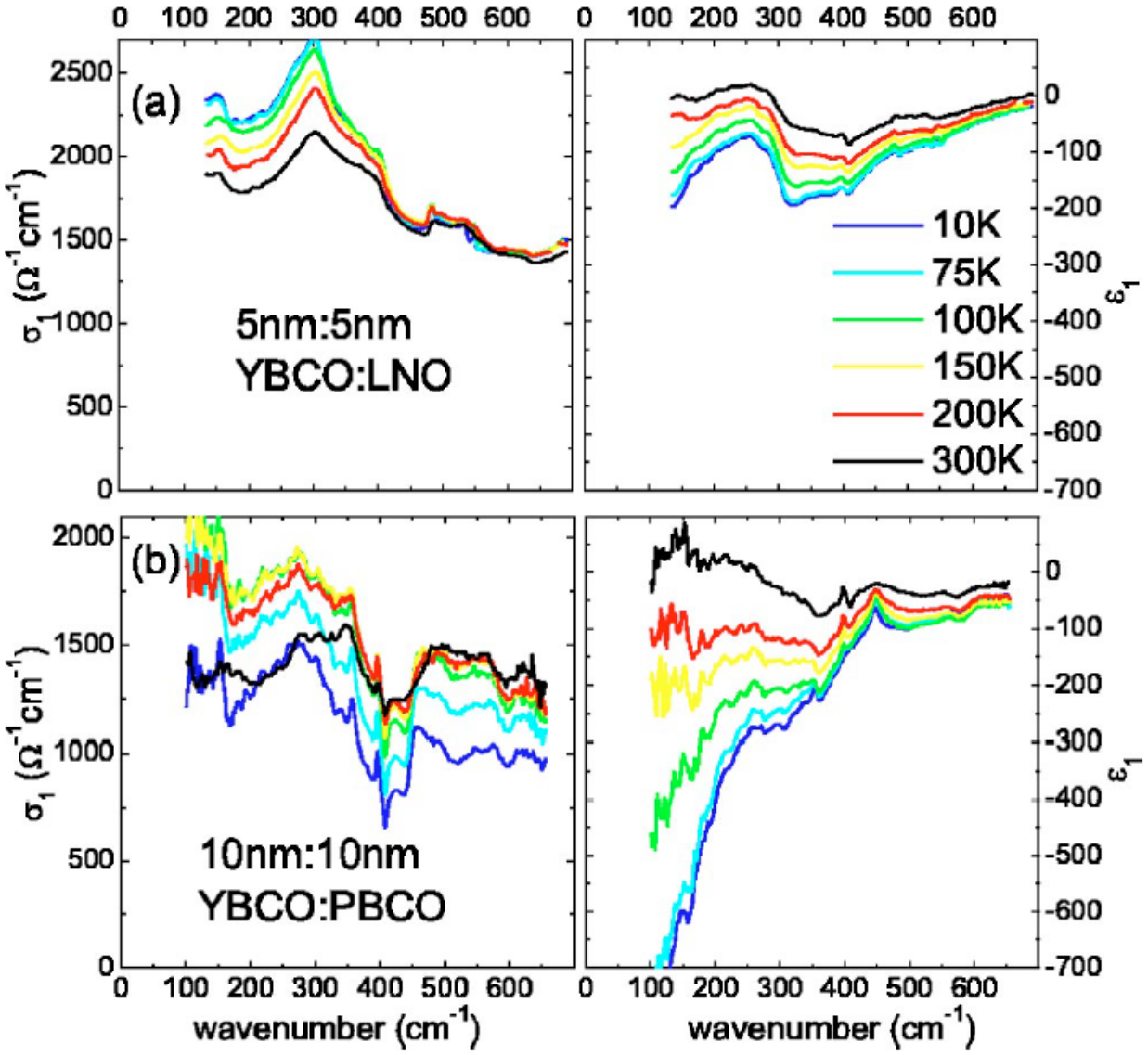
X-ray diffraction and TEM



[8nm YBCO x 6nm LCMO]$_{20}$

SO FAR c- AXIS ⊥ FILM PLANE ONLY

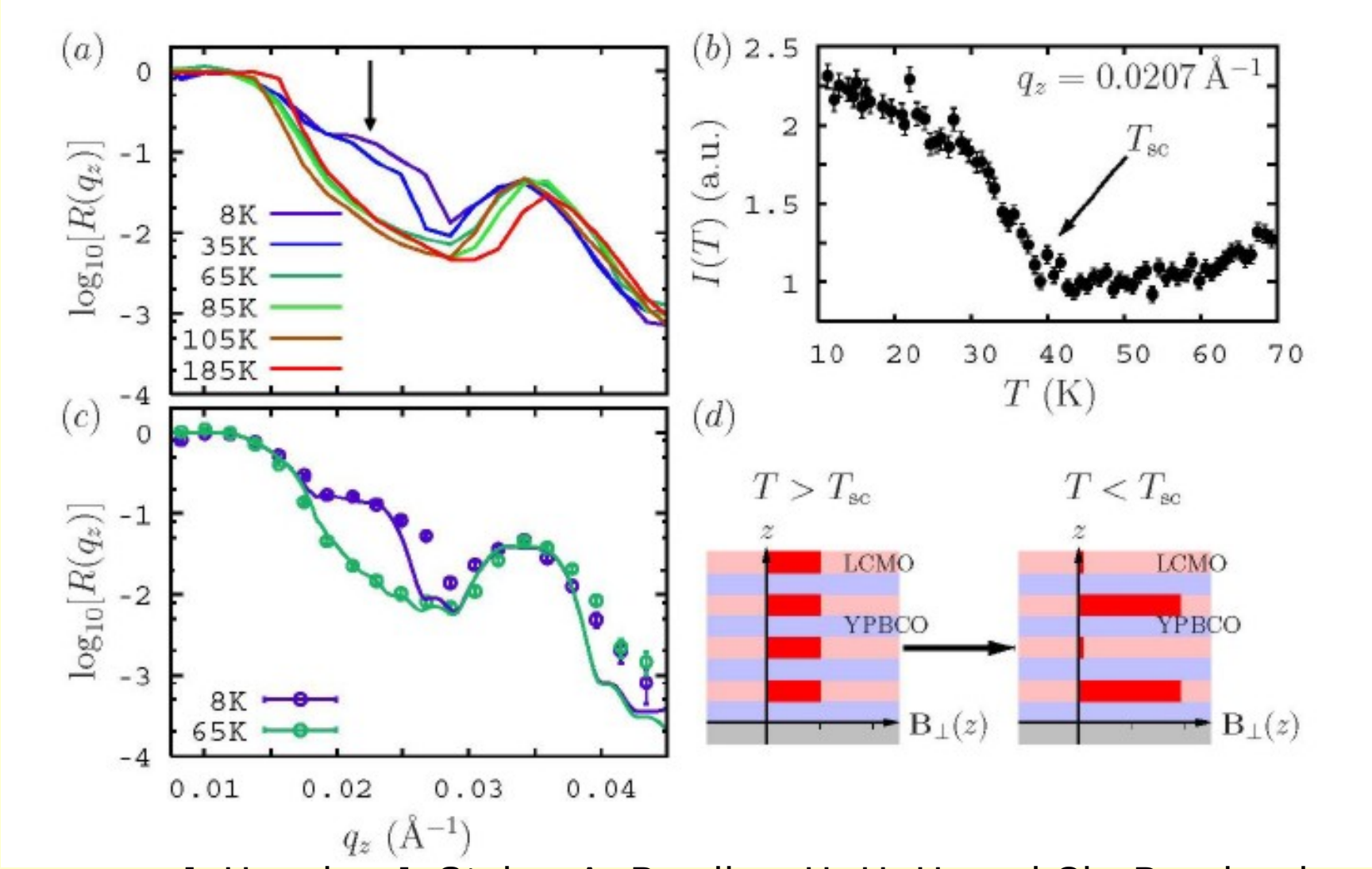
PHYSICAL REVIEW B **69**, 064505 (2004)



$YBa_2Cu_3O_7$/
$LaNiO_3$

$YBa_2Cu_3O_7$/
$PrBa_2Cu_3O_7$

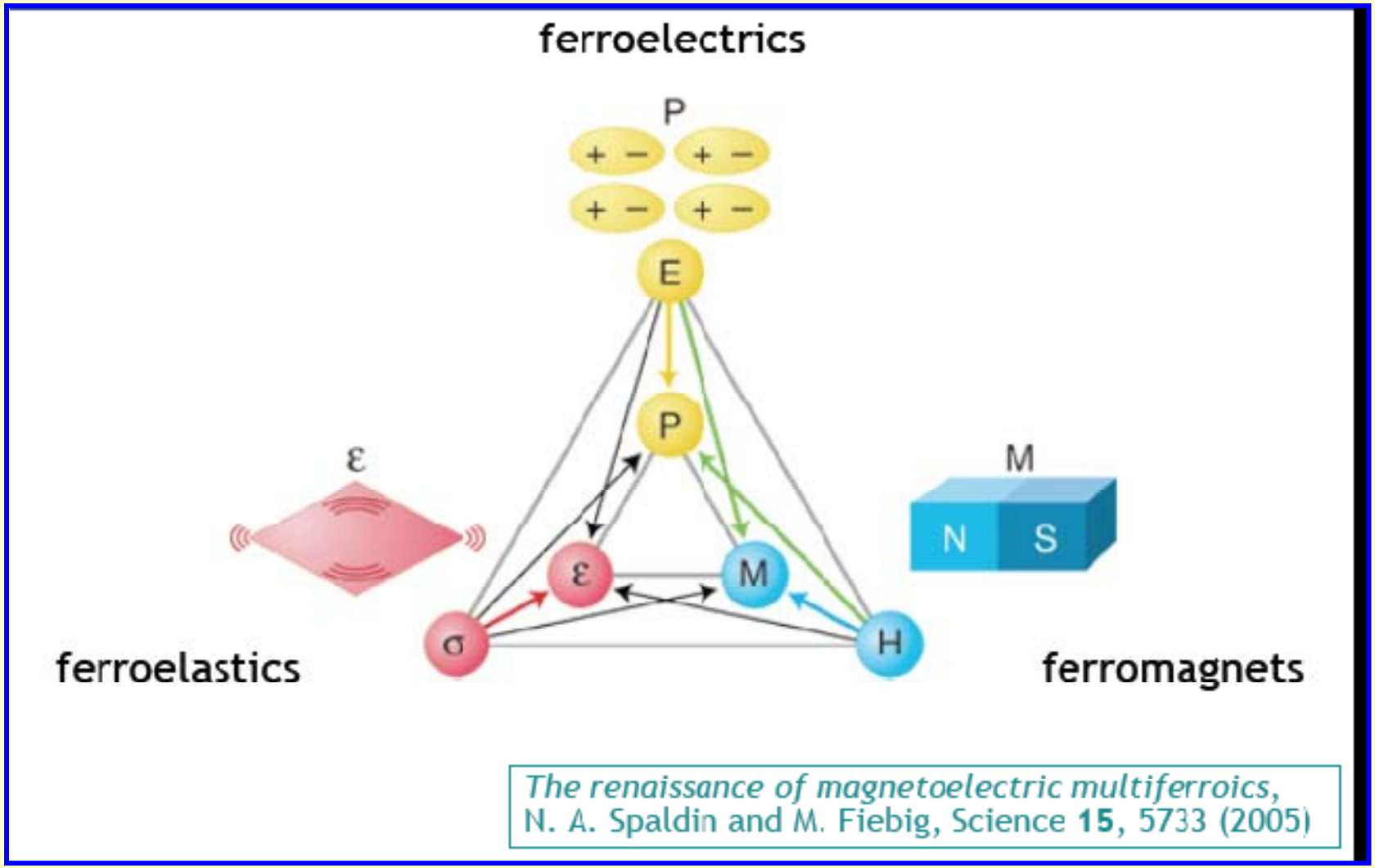
BRAGG PEAK AT (1/2)th ORDER IN $Y_{.6}Pr_{.4}Ba_2Cu_3O_7$/ LCMO SUPERLATTICES



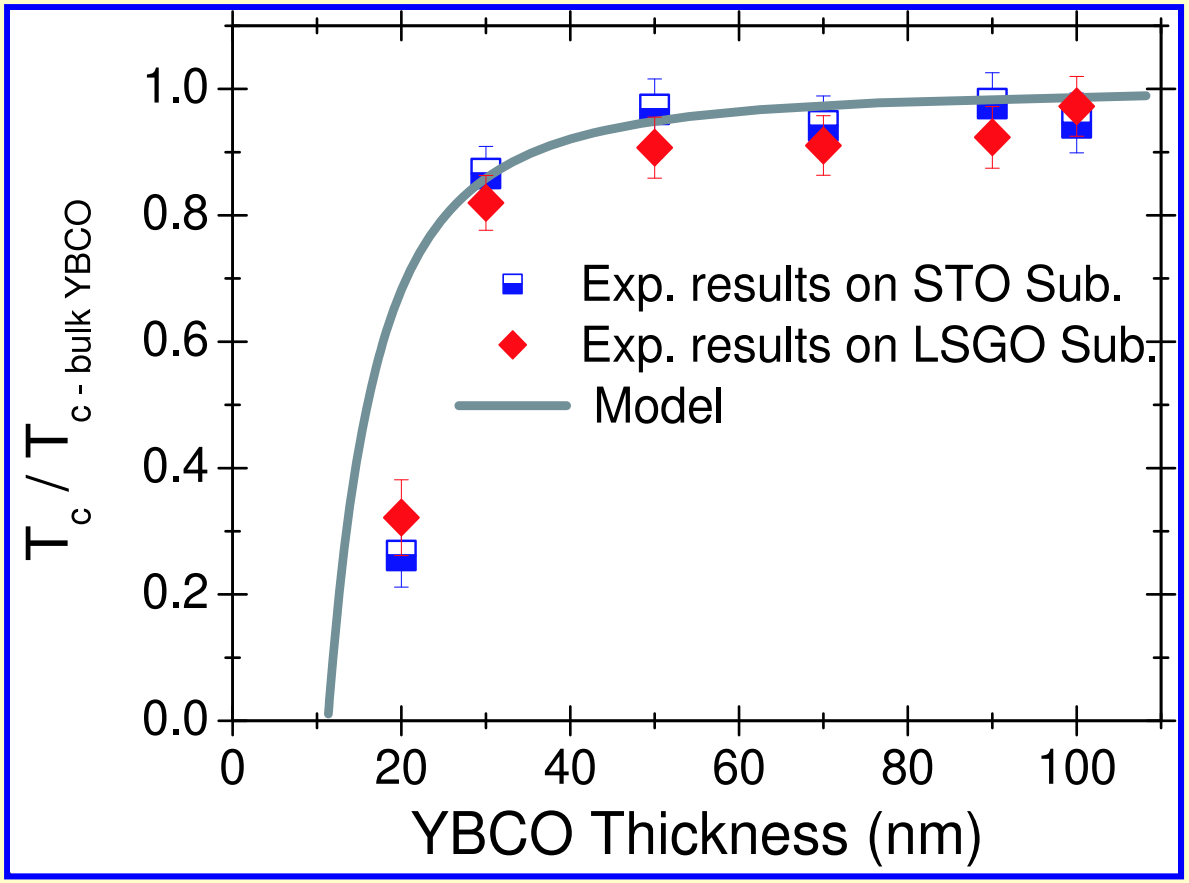
J. Hoppler, J. Stahn, A. Buzdin….H.-U. H. and Ch. Bernhard

submitted to Nature 2007

MULTIFERROICS



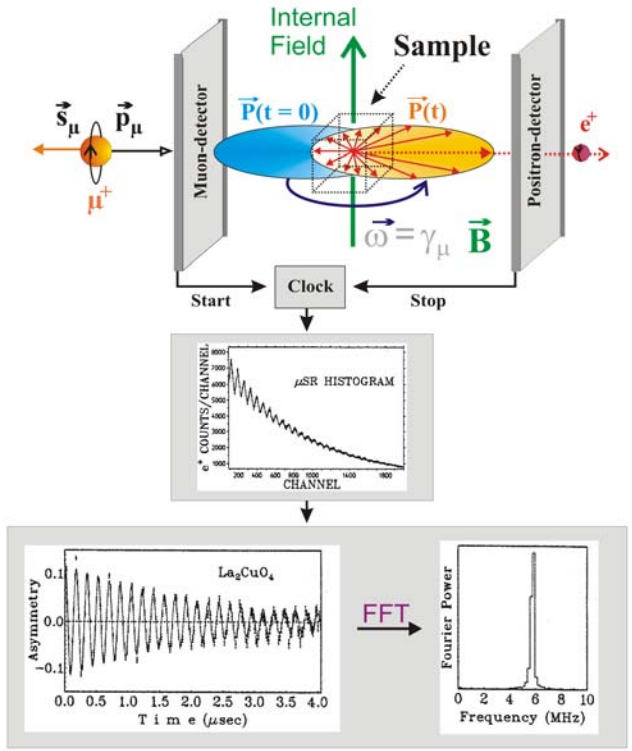
$$d = \alpha \xi_{FM} \cong 3.7 \frac{\alpha m^* \hbar v_F^2}{\Delta(0) \Delta E_{ex} n_{qp}(0) e^2} \frac{\sqrt{T/n_{qp}(T)}}{\sqrt[4]{1-(T/T_c)}}$$

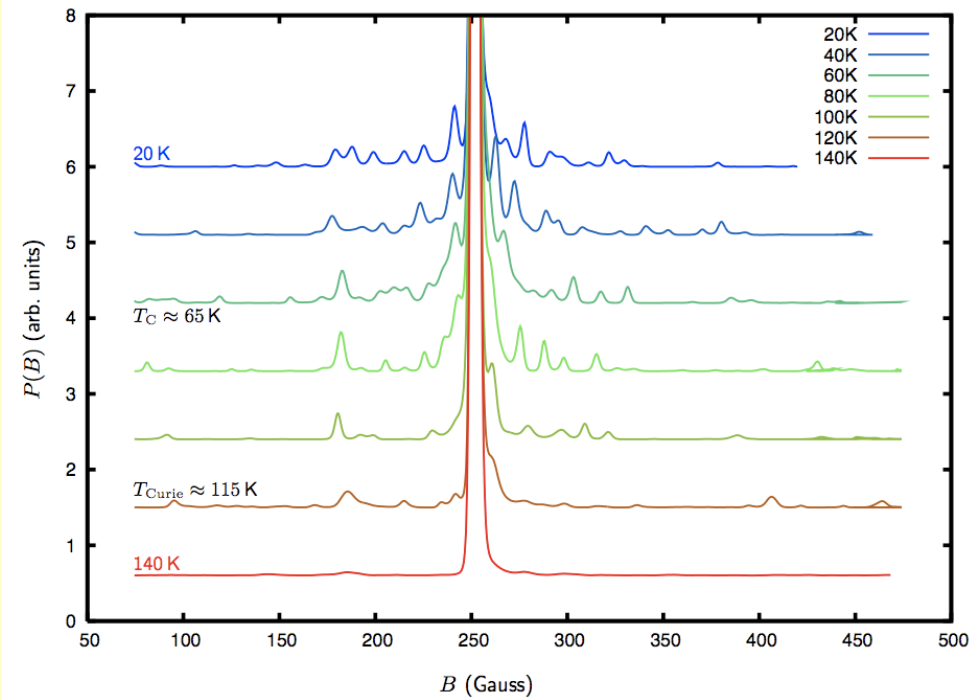


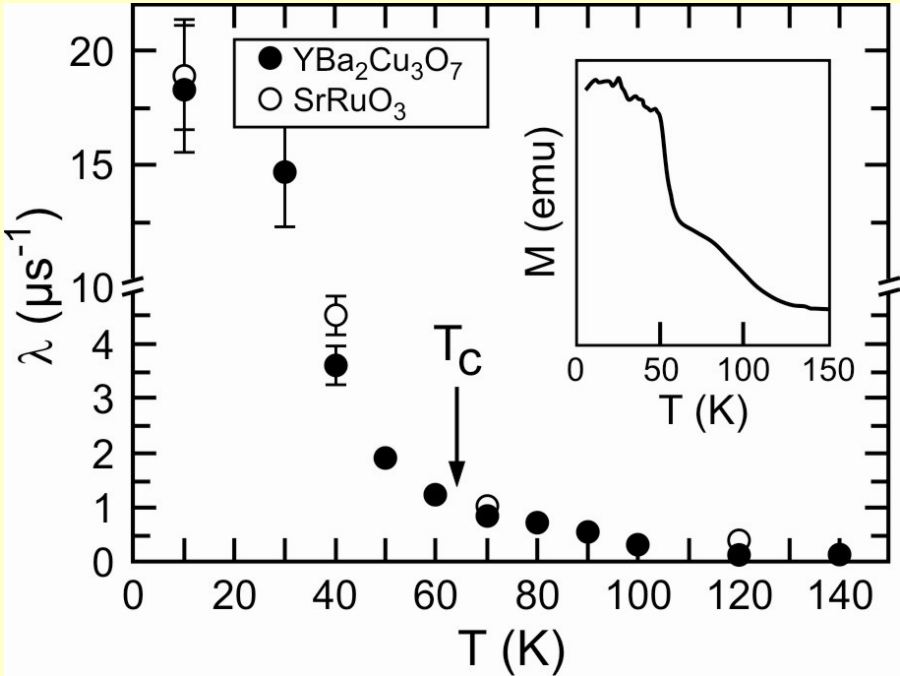
S. Soltan, J. Albrecht, H.-U.H. PRB 70 (2004) 144517

Technique

Zero-Field Muon Spin Rotation



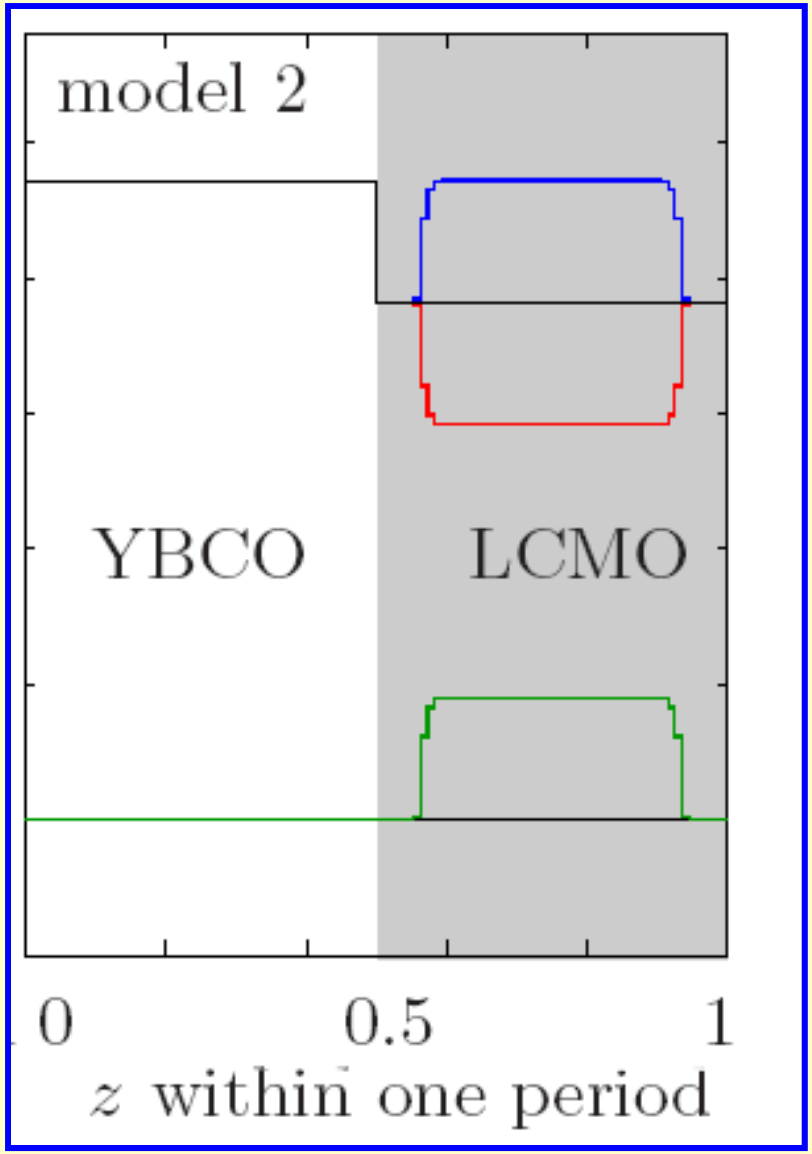




C. Bernhard et al
unpublished

SUCCESSFUL MODELS

"DEAD" LAYER MODEL

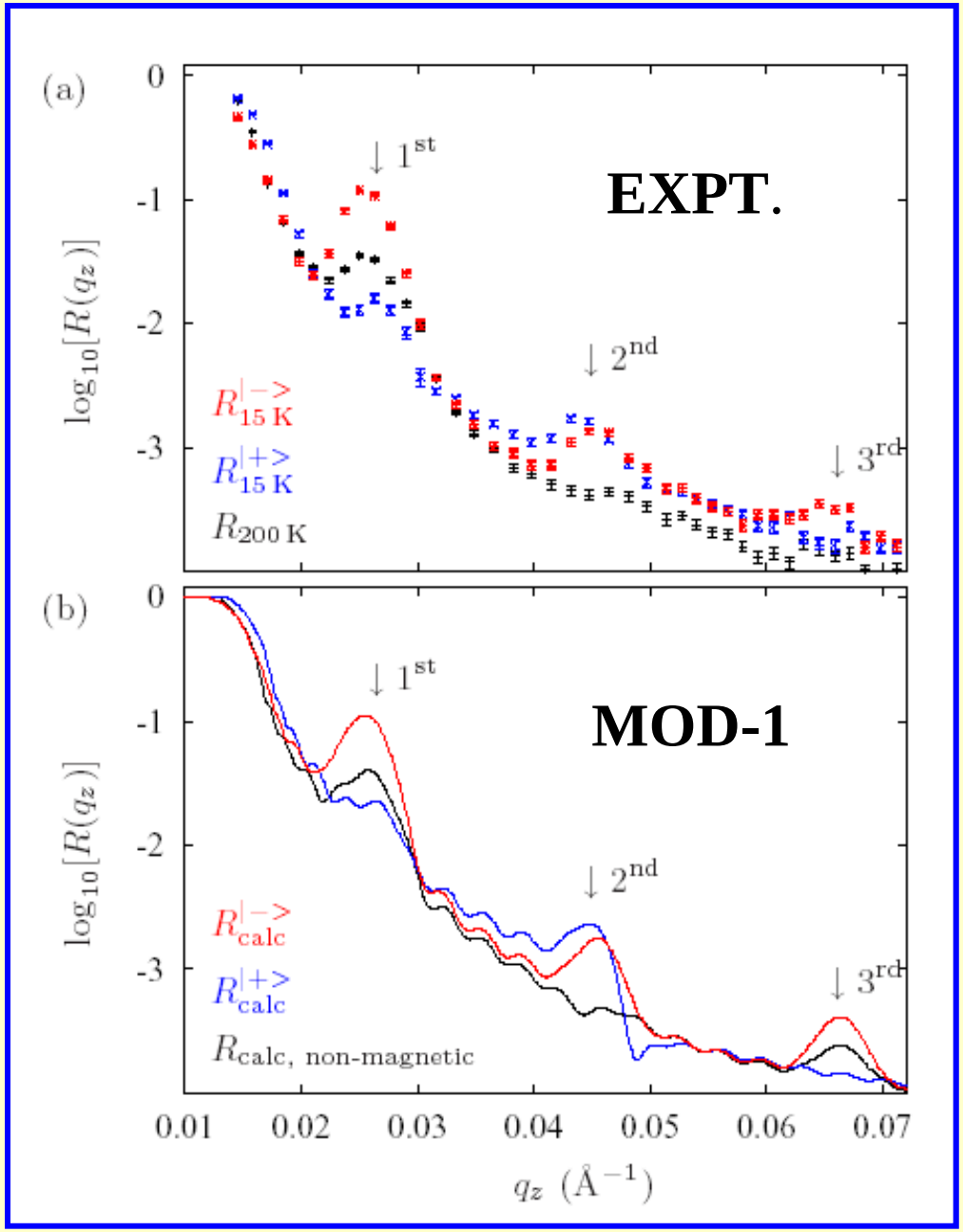


Region with no net magnetic moment in LCMO

Due to

* **interfacial strain**
* **charge transfer**

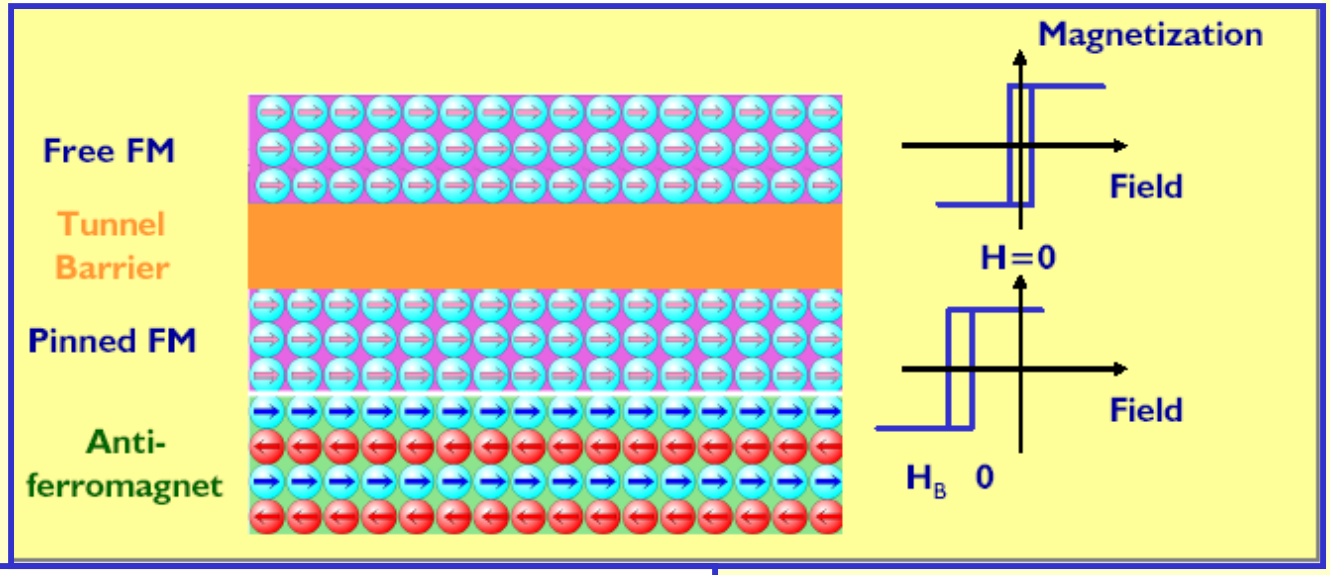
COMPARISON OF EXPERIMENT AND MODEL

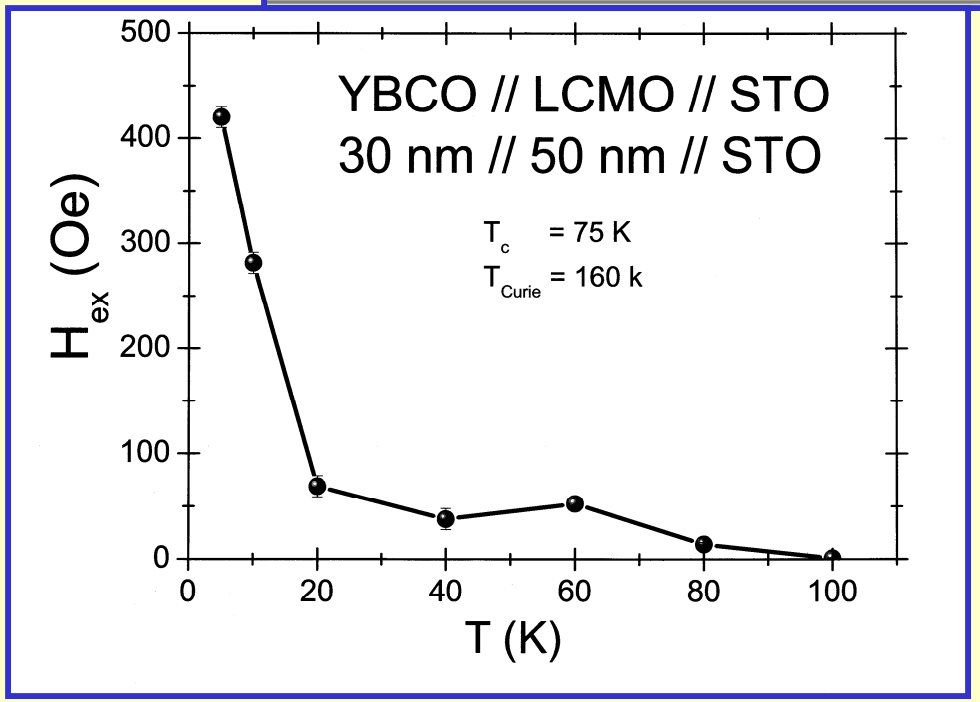


BOTH MODELS CAN MIMICK THE EXPERIMENTAL RESULTS !!

GENERALLY: FM / AFM INTERFACE CAUSES EXCHANGE BIAS EFFECTS

EXCHANGE BIAS FM / AFM INTERFACE



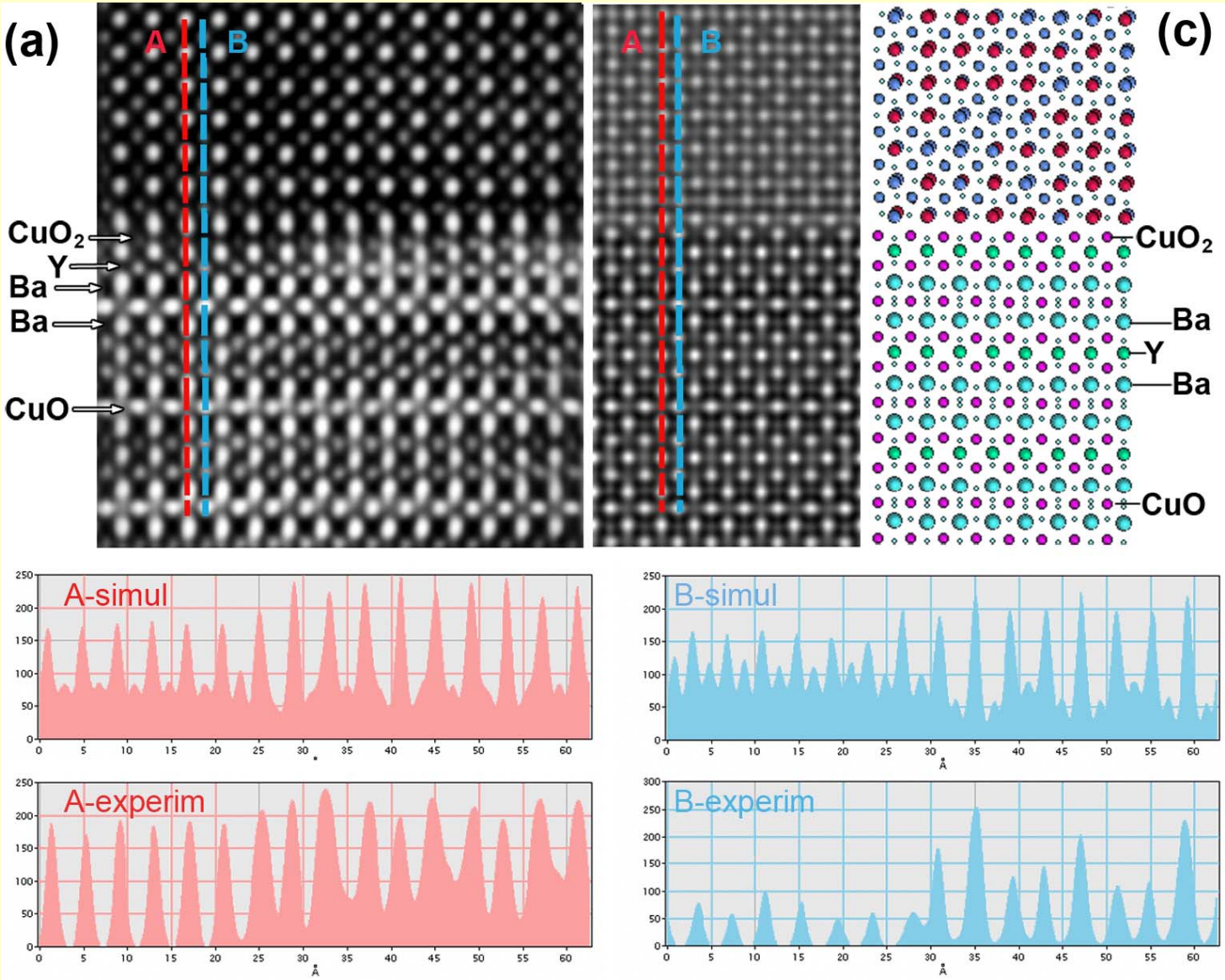


ANTIFERROMAGNETIC COMPONENT OF THE MAGNETIZATION PROFILE AT THE YBCO / LCMO INTERFACE

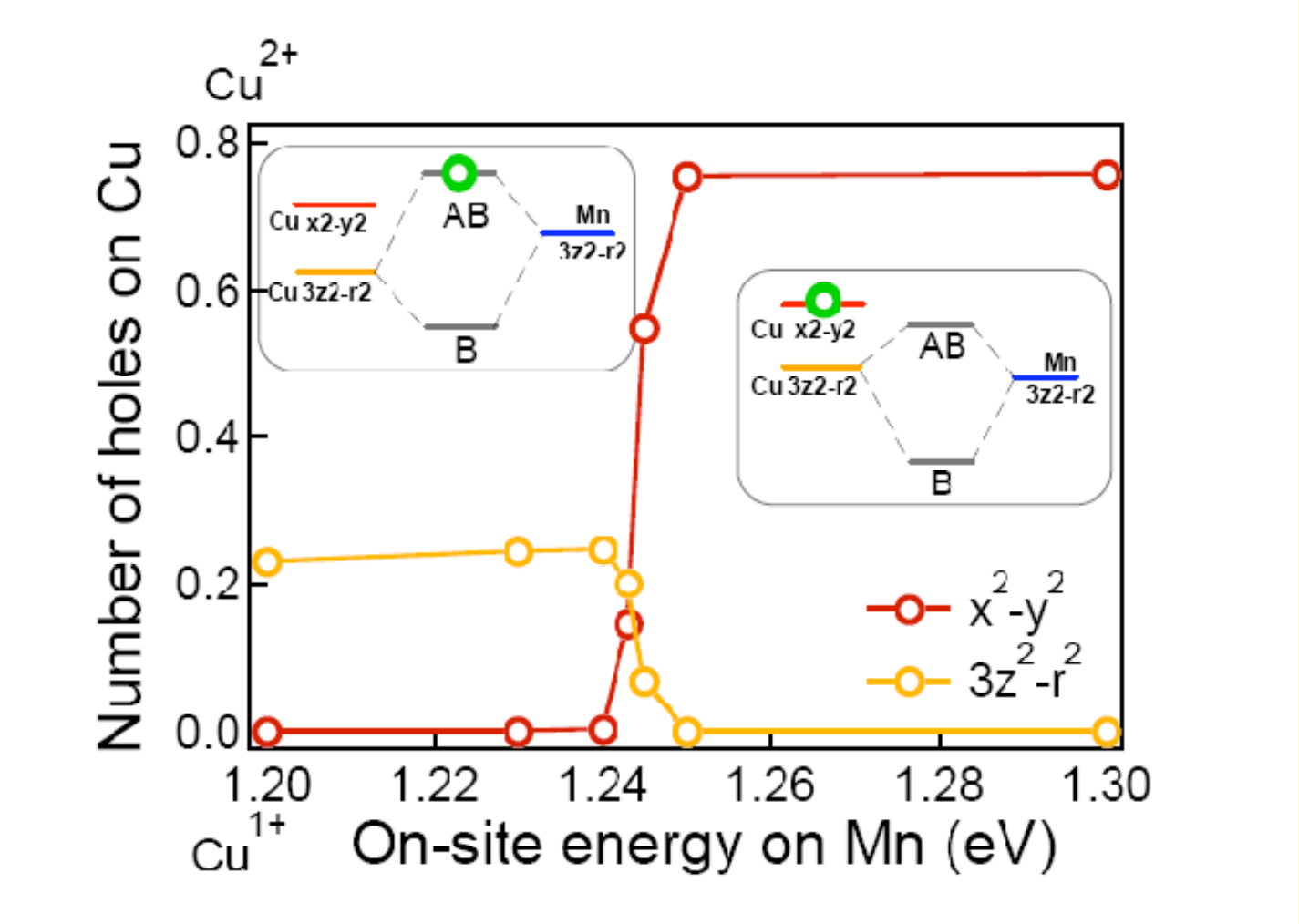
H.-U. H., S. Soltan, J. Albrecht et al. to be published (2007)

N. Haberkorn et al. APL 84 (2004) 3927

ONCE IS NEVER TWICE IS EVER



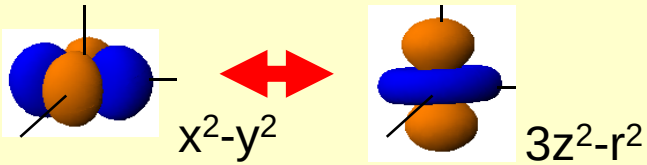
O. I. LEBEDEV October 2007



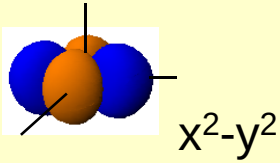
Occupancy of Cu d-orbitals at the LCMO-YBCO interface as a function of Mn hole on-site energy, as predicted by the exact diagonalization calculations.

J. Chakhalian ,J.W. Freeland, H.-U. H., G. Cristiani,G. Khaliullin, M. van Veenendaal, and B. Keimer Science 2007

assume bulk orbital occupancy is maintained at interface



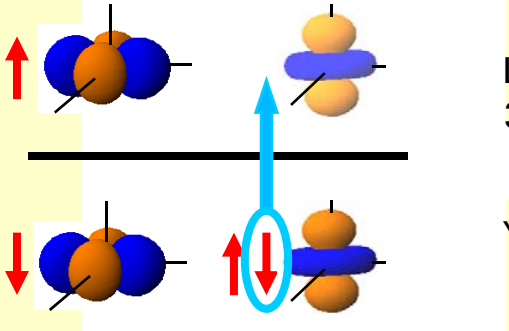
metallic LCMO: fluctuating orbital occupancy



metallic YBCO: x^2-y^2 orbital occupied

→*ferromagnetic* exchange coupling across interface inconsistent with experiment

orbital reconstruction at interface

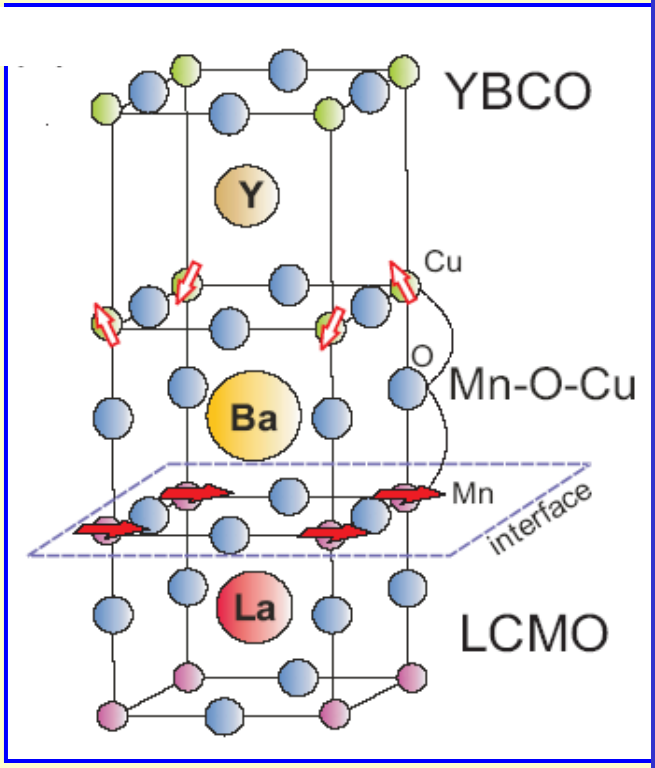


LCMO:
$3z^2$-r^2 orbital depleted

YBCO:

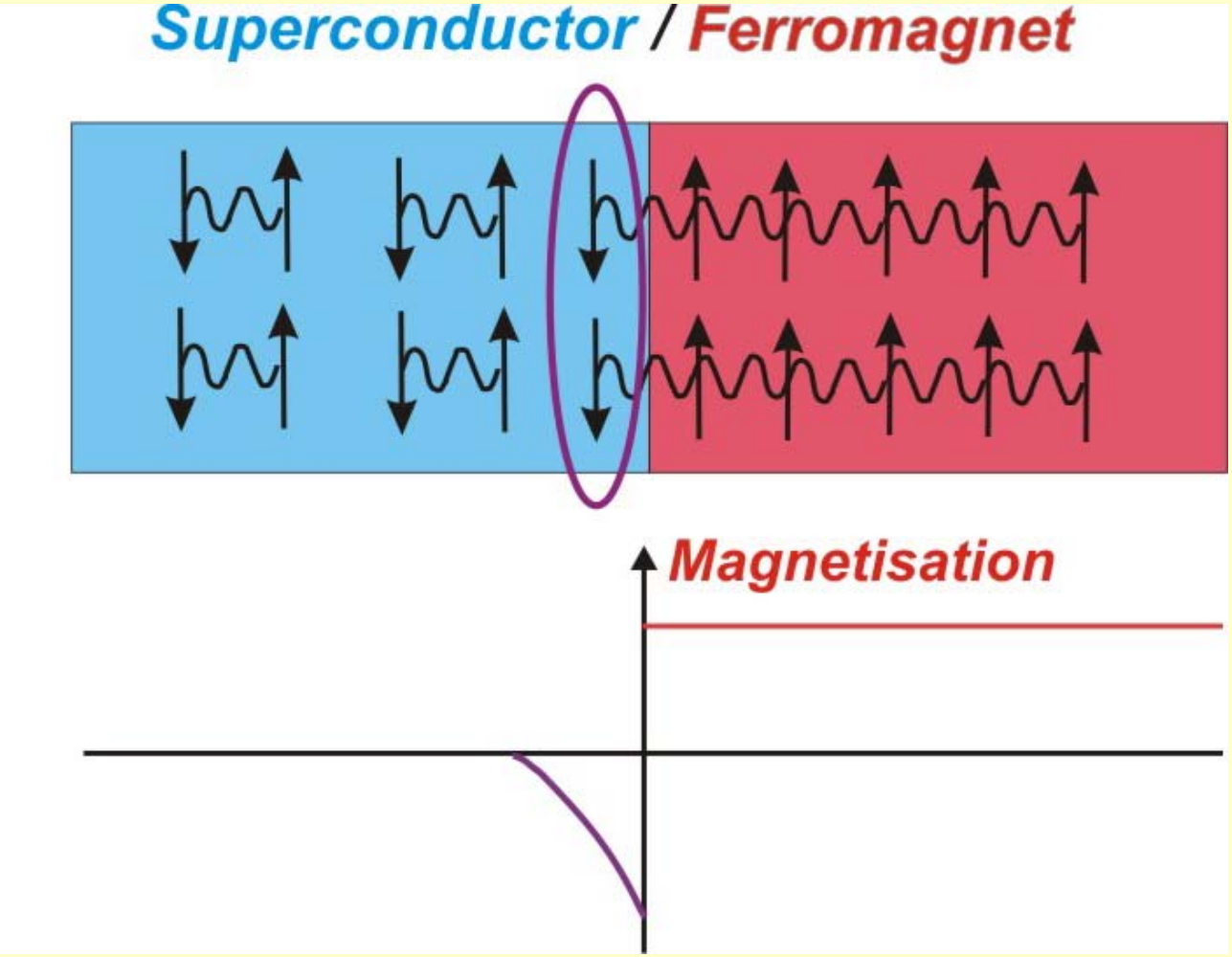
Superexchange interaction across interface

→ *antiferromagnetic* coupling, as observed



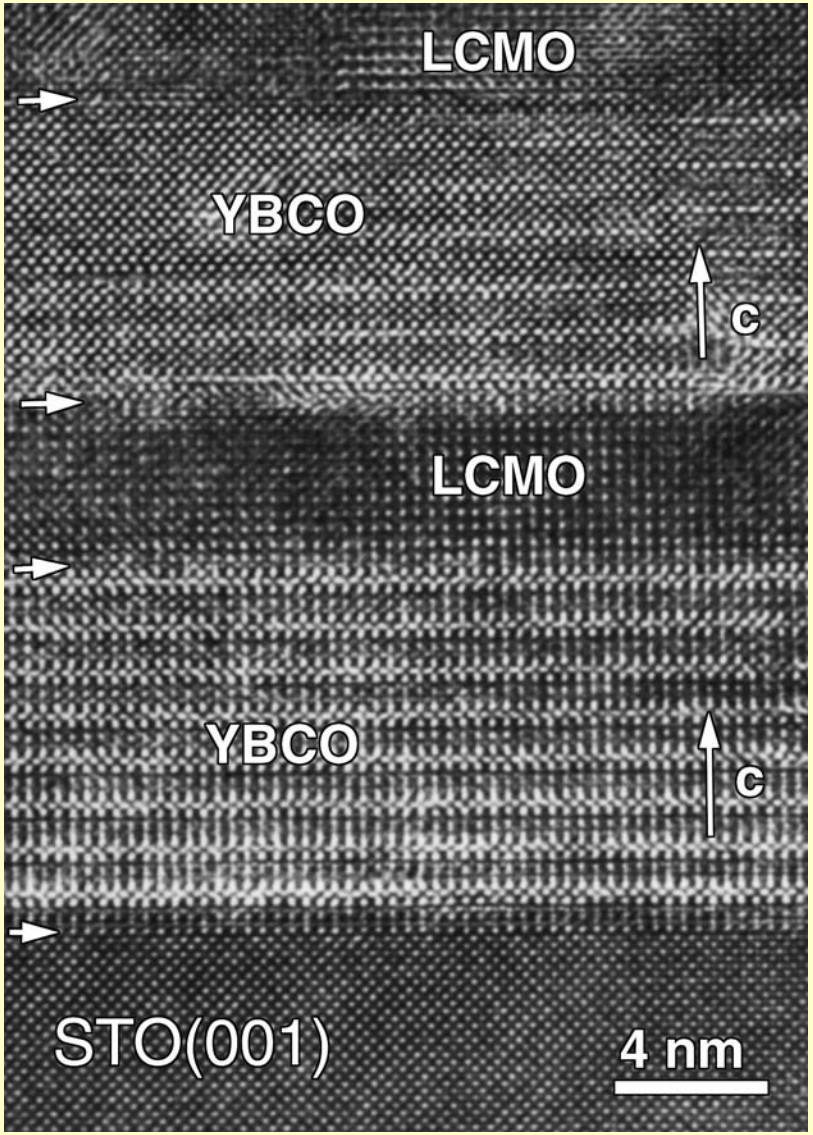
J.Chakhalian, J. Freeland, H.-U. H. et al. Nature Physics 2(2006) 244

Proximity effect between spin singlet and FM

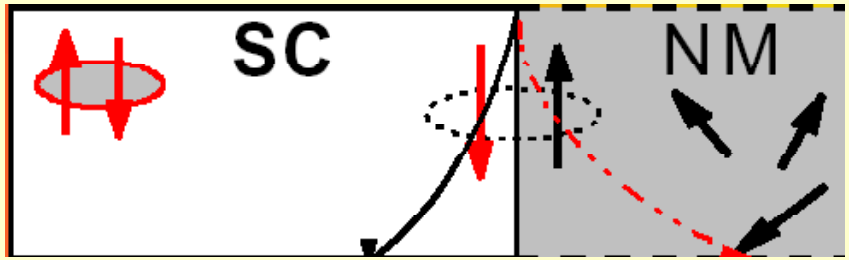


F.S. Bergeret, Phys. Rev. **B 69**, 174504 (2004).

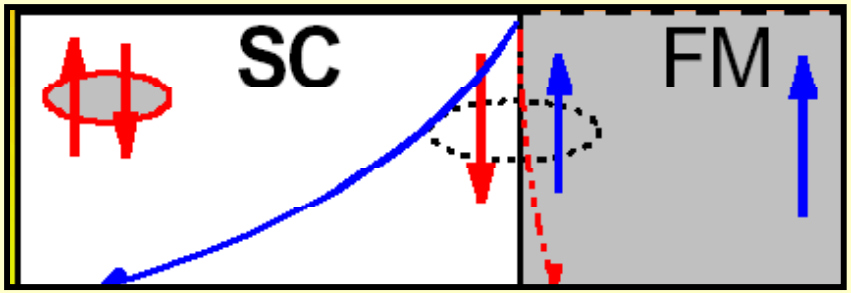
HRTEM YBCO /LCMO



INTERFACE PROPERTIES DOMINATE "BULK" PROPERTIES



$$\zeta_{NM} = (D_{NM} / 2 \pi T)^{1/2}$$



$$\zeta_{FM} = (D_{FM} / J)^{1/2}$$

SELF - INJECTION FROM FM SIDE

$$\Delta_{qp}/\Delta(0) = 1 - 2n_{qp} / 4N(0)\,\Delta(0)$$

RECENT RESULTS

EMBEDDED INTO A GENERAL FRAME